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CANAL RAY* AND ELECTRON EXCITATION OF THE BAND SPECTRUM OF NITROGEN

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Abstract

The idea is suggested that the excitation of band spectra by canal ray* impact on the one hand, and by electron impact on the other, may give quite different intensity distributions. The results of three groups of experiments on the band spectra of nitrogen are presented.

In the first, the relative intensities of the lines in the 3914 negative band were studied. There seemed to be a small weakening of the lower rotational lines in the canal-ray excitation compared to electron excitation.

In the second, the relative intensities of the second positive group and of the negative group were observed in a canal-ray beam. The intensities of the transitions from high initial vibrational states were abnormally great. The variations in comparison plates taken by us and by others with various sources were so great that no satisfactory standard of comparison could be chosen as representing excitation purely by electron impact.

This suggested the third phase of the work, a study of the excitation by a beam of 700 volt electrons. This gave a most unusual distribution of intensity with nearly all the energy in the 0→0 and 0→1 bands of the negative group and a similar concentration in the second positive group.

Introduction

THE theory of the relative intensities of the lines in a band and the bands in a system has been rather fully developed.[1] There is no need to reproduce it here in detail but we may recall one guiding principle, that due to Franck and Condon. According to this notion an electron striking a molecule can alter only the electronic configuration without having any direct effect on the vibration or rotation of the nuclei.

Initially, the authors were interested in a case where this principle certainly should not apply, namely, excitation by canal ray* impact. In such a case the impacting ion might be expected to transfer both angular and vibrational momentum to the molecule being excited and consequently to produce a different distribution of intensity from that observed with pure

* The term "canal ray" is used throughout this paper to include both the positive ions and high speed neutralized molecules that emerge behind the perforated cathode of a discharge. It seems better to restrict the term positive ray to ionized molecules.

[1] See Mulliken, Revs. of Modern Phys. **2**, 79 (1930) and references cited there.

electron excitation. It might be expected, therefore, that, in a given band, the higher rotational members of all branches would be relatively stronger than when excitation was by electron impact and, similarly, that, in a given system, the bands corresponding to higher initial vibrational states should be relatively stronger than when excitation was by electron impact. A search for such effects was undertaken.

The bands of nitrogen were chosen for examination because more is known about them than about the bands of any other gas of equal experimental convenience. There have, of course, been many studies of the excitation of spectra by canal rays and in particular the bands of nitrogen have been studied. But the point of view was so different from our present one that no very satisfactory evidence on intensity distribution is available. Detailed discussion of previous work will be more intelligible later on in connection with our own results.

But the earlier work did suggest what we found to be the case, namely that the intensities are not strikingly different from those usually published and ascribed to pure electron excitation. It became necessary therefore to examine these "electron excitation experiments," considering carefully the evidence on relative intensities and their variation with varying conditions of source. For example, Birge gives a set of intensity estimates on the second positive nitrogen bands. He says[2] this illustrates "the most common type of intensity distribution." Yet in a footnote he says "the relative intensity of the bands in this system is very sensitive to changes in self-induction, capacity and other experimental conditions. Hence it is very difficult to give a normal intensity distribution." Yet he does treat this particular distribution as the "normal" intensity distribution and proceeds on this basis. For the sake of convenience we will also speak of this particular distribution as "normal." Birge has apparently studied deviations from this "normal" intensity considerably but his only reference[3] is to a fifteen line abstract and we can find no complete account of his investigations. Fortunately, other authors are not so hesitant about publishing their results and theories, imperfect though they be. Herzberg[4,5] in a series of papers has given an excellent account of the variations of intensity distribution in the nitrogen bands under different conditions of excitation and the factors to be considered in accounting for the observations theoretically. However, in all his experiments he used an electrodeless discharge so that it is difficult to say exactly what the conditions of excitation were. Apparently the only experiments where the excitation was certainly by single electron impact were those whose object was to determine the critical potentials of various band systems.[6] Consequently the electron speeds used were low.

Both in Birge's "normal" case and in those reported by Herzberg the intensity distribution is of the type predicted by theory. That is, if the

[2] Birge, Molecular Spectra in Gases, Bull. Nat. Res. Council, **57**, 135 (1926).
[3] Birge, Phys. Rev. **25**, 240, 1925.
[4] Herzberg, Ann. d. Physik, **86**, 189 (1928).
[5] Herzberg, Zeits. f. Physik **49**, 761 (1928).
[6] See references 16, 17, 18.

system is arranged in a square array with the bands of the same initial vibration state all in the same row and the bands of the same final state all in the same column (See Tables I to IV), the most intense bands lie on a parabola whose vertex is toward the 0→0 band and whose shape depends on the nuclear binding in the initial and final electronic states. The distributions differ only in rate of falling off of intensity with increasing distance from the vertex of the parabola. This is just the kind of effect we may expect from canal-ray excitation. It is clear, therefore, that control experiments with electrons must be made before any conclusions can be drawn from those on canal rays. Furthermore experiments with electrons are of importance for direct comparison with theory. This, then, became the secondary object of our work.

Though our experiments have suffered many interruptions and are by no means complete, we believe them of sufficient importance to report. We feel this the more strongly because we are convinced that progress in this field has been retarded by the substitution of abstracts, footnotes and "private communication" for frank and full publication.

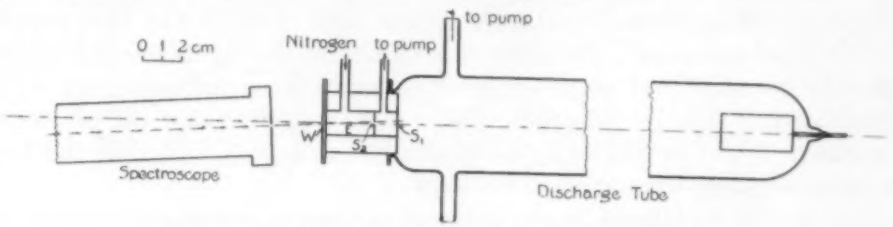

Fig. 1. Schematic diagram of canal ray apparatus.

CANAL RAY EXCITATION

First experiments

At the Chicago meeting of the Physical Society last November we reported[7] the results of shooting canal rays from a mixture of nitrogen and mercury into an atmosphere of nitrogen. The apparatus, Fig. 1 and Fig. 2 (a), consisted of a cylindrical discharge tube into the end of which a brass water-cooled cathode was sealed with wax. The slits S_1 and S_2 behind each other in the cathode defined a canal-ray beam which shot into the space E in front of the quartz window, W. Nitrogen generated from ammonia and bromine and stored over P_2O_5 flowed continually into the chamber E and out through the slits and the evacuation tube between the slits. The discharge contained mercury at approximately room temperature and a certain amount of nitrogen that diffused through the slits. The discharge was run with a 15,000 volt transformer and with a kenotron in circuit for rectification. Pressure and voltage conditions were varied until a fairly intense canal ray beam appeared; the pressure of nitrogen finally used was of the order of 0.04 mm in the space E. In these early experiments there was sometimes a certain amount of secondary discharge within the cathode. In taking photographs the spectroscope was set at a slight angle to the beam as shown in Fig. 1. This angle had to be very small to get good intensity yet large enough so

[7] Smyth and Arnott, Phys. Rev. **35**, 126, 1930.

that no light came through the slits S_1 and S_2 into the spectroscope. The difficulty of this adjustment and the occasional secondary discharge made these preliminary results less reliable than later ones since the spectrum photographed may not have been entirely due to canal-ray excitation.

Photographs were made first with a constant deviation small glass Hilger instrument and then with a small one-meter concave grating. The plates made with the prism spectroscope covered the region from about 4900 to 3900A.U. with sufficient intensity and resolving power for the study of the bands of the second positive and the negative groups which lie in this region. The lines in the bands were not resolved but in the stronger bands the positive (R) and negative (P) branches were separated. In the grating spectra, in the second order, all the lines of the R and some of those in the P branch were resolved. In both cases very long exposures of the order of 30 to 80 hours were required to bring out any considerable intensity. Ilford Panchromatic plates were used with the prism spectrograph and Eastman Panchromatic films with the grating.

The first photographs taken with the prism instrument showed both negatve and second positive bands present with the 4278 and 3914 negative bands predominating. The relative intensity of the bands seemed approximately "normal" but there appeared to be an abnormal separation of the positive and negative branches. These facts suggested that the vibrational intensity might be the same as in electron excitation but that the lower rotational states were abnormally weak.

Attention was therefore concentrated on getting grating photographs and then making exact measurements on the relative intensities of the lines in the bands 3914 and 4278. Photographs were also made with an electrodeless discharge and compared with the canal-ray plate both visually and with a densitometer; the results of Fassbender[8] and of Ornstein and van Wijk[9] were also compared. The experimental result seems to be a small but definite weakening of the lower rotational transitions in the canal-ray plate. This was the stage of the work reported at Chicago. Since that time we have been more meticulous about our conditions of excitation and avoidance of light from the main tube, as we will describe presently. Unfortunately this made it impossible to get photographs with the grating even with exposures of as much as 72 hours and therefore no further quantitative evidence is available on the relative intensities of the lines in a single band.

Searching the older work, we find the published reproductions of Fulcher[10,12] and of Rau[11,12] have sufficient resolution to show the fine structure of the 4278 band. Fulcher's is the clearer picture and looks very much like ours, but the problem needs more accurate experimental work before any certain conclusion can be drawn.

[8] Fassbender, Zeits. f. Physik **30**, 73 (1924).
[9] Ornstein and van Wijk, Zeits. f. Physik **49**, 315 (1928).
[10] G. S. Fulcher, Astrophys. J. **35**, 101 (1912).
[11] H. Rau, Ann. d. Physik **73**, 266 (1924).
[12] Wien-Harms, Handbuch der Exp. Phys. XIV, p. 687, and p. 690.

Later experiments

A number of changes were now made in the apparatus. A General Electric high potential set made up of transformer, kenotrons, condensers and resistances and supposed to give a constant potential was substituted for the transformer. This meant that the canal rays would now be of nearly uniform energy instead of having energies ranging from zero to the maximum voltage of the secondary of the transformer. The other principal change was in the mounting of the discharge tube which was tilted until at an angle of about thirty degrees from horizontal. This made it possible to head the spectroscope directly at the canal ray beam without its receiving any light through the slits S_1 and S_2 from the discharge tube. To prevent reflected light from getting into the spectroscope the inside of the cathode was painted black. There were some further minor modifications in the cathode which need not be described. The new set-up is shown in Fig. 2 (b).

This new outfit ran very much more smoothly than the old as long as no more than a few milliamperes were drawn from the high potential set.

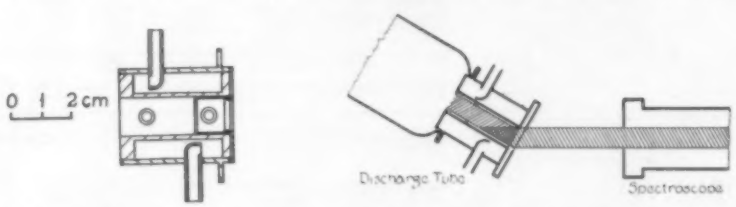

Fig. 2. (a) Details of water-cooled cathode. (b) Second arrangement of tube and spectroscope.

At such currents and with a voltage of 5000 it was possible to get a clearly defined beam which seemed just about as bright as the one we had been using. Nevertheless we were unable to get more then a few mercury lines on any spectra taken with the grating.

Returning to the small glass instrument several satisfactory spectra were obtained. They were very similar to those obtained before showing the same wide separation of positive and negative branches in the 4278 band, but showing a slightly higher intensity in the higher vibrational bands. It was obviously desirable to cover a greater range of the spectrum than was possible with this instrument so a Type E315 Quartz Hilger spectroscope was tried. The first photograph was a little overexposed but the second was very satisfactory. It was an exposure of fifty hours during which the tube ran perfectly steadily at a voltage of 5500 to 6000 with a pressure of 0.04 mm of nitrogen in the cathode and a sharply defined bluish canal-ray beam reaching without scattering to the quartz window.

This plate covered the spectrum range from $\lambda = 5790$ to $\lambda = 2100$, but above 4708 there was very little on it and the dispersion was small. Measurements and densitometer records were made of this entire plate. Besides the negative and second positive groups of bands it showed many mercury lines and many nitrogen spark lines. As impurities there were the resonance lines of Al and Cu and a few other Al lines. These might all be expected since the

main part of the cathode was brass but with an aluminum disk over the front of it to reduce sputtering. Unexpected and unaccounted for were a

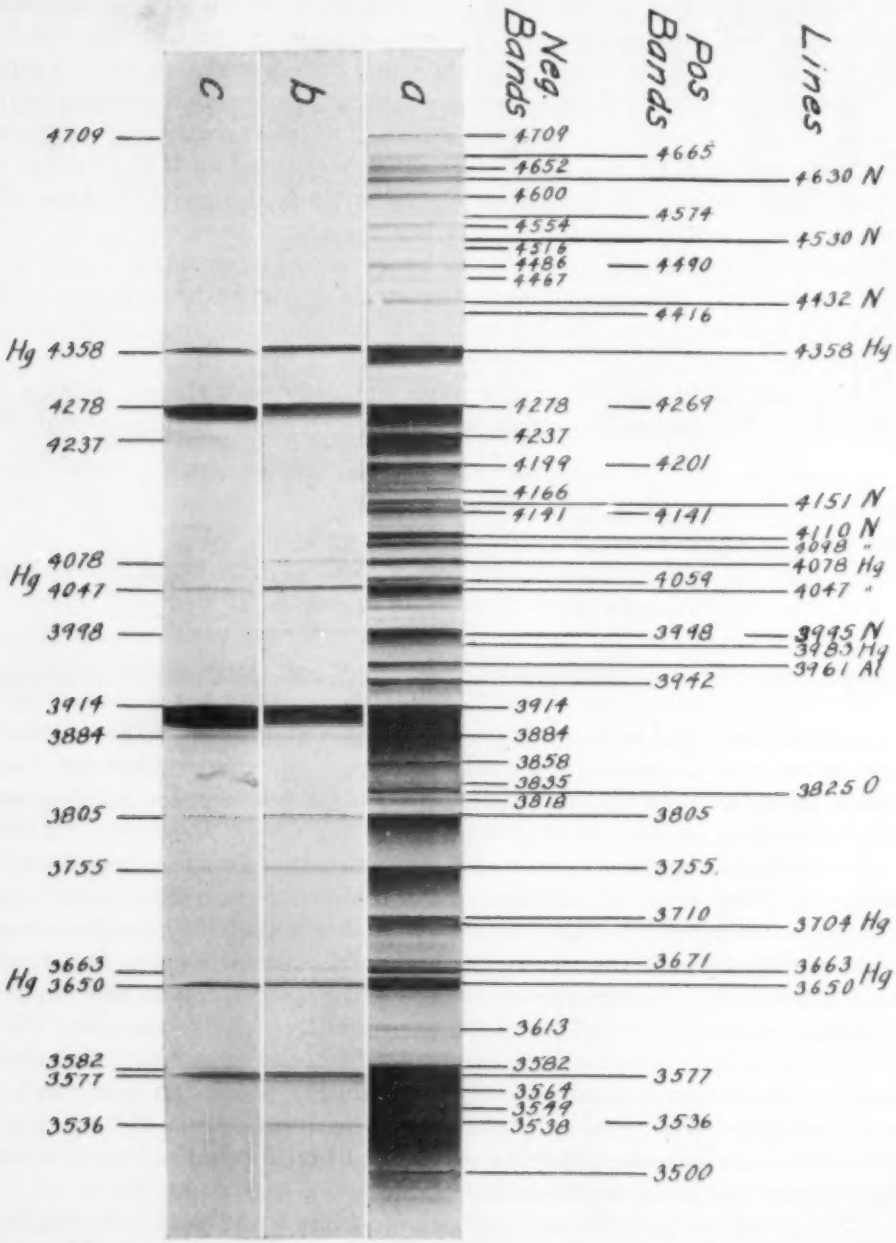

Fig. 3. Spectrograms taken with E315 quartz Hilger spectroscope. (a) Canal ray beam (5500 volts). (b) Discharge used as source of canal rays. (c) Electron beam (700 volts).

number of oxygen lines chiefly below 3000A.U. Finally there were a few faint bands in the neighborhood of 2500 which may have been the fourth positive group of nitrogen.

In Fig. 3 (a) a section of this plate is reproduced. The print is a little over exposed to show some of the fainter bands, in particular the one at 3613. From a study of this plate and the densitometer records of it, it was possible to estimate the intensity of most of the bands of both the second positive and the negative groups. In some cases the resolution was so poor that an estimate was dubious or impossible. This is indicated in the tables below which give the results of visual and densitometer estimates of the relative blackening of the photographic plate.

TABLE I. *Densities of second positive group. Canal-ray excitation plates.*

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	3371 18	3577 11	3805 12	4059 8	4344 *	4666 4				
1	3159 15	3339 3	3536 6*	3755 12	3998 10*	4269 *	4574 00			
2	2977 12	3136 14	3309 6*	3500 4	3710 10	3942 9	4201 *	4490 4*		
3	2820 2*	2962 12	3116 10	3284 6	3469 1	3671 7	3894 *	4141 *	4416 1	
4		2814 4	2953 12	3104 7	3268 6	3446 0	3642 4	3857 *	4094 *	4356 *

* Wholly or partially obscured by another line or band.

Considering first the second positive group one could hardly ask for a more perfect parabolic intensity distribution. In general it agrees very well with the intensities given by Birge. One curious point is the extreme weakness of the 4574 band. This is confirmed by the other plates taken with this type of excitation in contrast to the comparison plates but we have no explanation for it. Looking for the effect we expected, an enhancement of the bands coming from the higher initial states of vibration, we find nothing very striking but a distinct tendency for the intensities in the 4th and 5th rows to be relatively stronger than in the figures published by Birge. They are also stronger than in our own comparison plates which will be discussed more fully below.

Turning to the negative bands, perhaps the most striking result is the presence of the "tail bands" first reported by Herzberg.[4] The strongest of these at 3613 is on the reproduction Fig. 3 (a) where it is hoped that the shading off to the red may be seen. It is very clear in the original. The band 4→0 at 2885A.U. is also identifiable on our plate, observed for the first time so far as we know. The absence of the higher sequences is presumably due to the low sensitivity of the plate in the region where they lie but had they been present they would not have been resolved.

The general run of intensities is very similar indeed to that given by

Herzberg,[5] for the case of strong excitation. Possibly in our case there is a slightly greater intensity in the lower rows of the table corresponding to higher initial vibrational states but certainly this is not sufficiently marked to be a proof of the effect we are seeking.

TABLE II. *Densities of negative group. Canal-ray excitation plates.*

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	3914 20	4278 15	4709 7							
1	3582 15	3884 12	4237 12	4652 7						
2	3308 7*	3564 12	3858 9	4199 10	4600 9					
3	3078 17	3299 8	3549 12	3835 6	4166 7	4554 6*				
4	(2885) (1)	3076 1*	3293 8	3538 10*	3818 8	4141 7*	4516 4			
5					3533 5*	(3807) *		4486 6*		
6									4467 5	
7										4459 *
8										
9										
10							2987 0	3174 0	3381 2	3613 7
11									3223 1	

* Partially or entirely obscured by other lines or bands. The band 14-10 at 3217 was also noted with intensity 0.

Nor does study of our own comparison plates strengthen our case. These were made with one spectroscope or the other with the following sources (a) a capillary Geissler tube discharge (b) the first transformer discharge used as a source of canal rays (c) an electrodeless discharge (d) the end of the positive column toward the cathode in the high voltage discharge finally

used as canal-ray source. Of these comparisons the first three all gave about the same results, the second positive group, as in Birge's "normal" distribution, was somewhat weaker in the lower rows than in Table I, while the negative bands were also perhaps a little weaker in the high initial vibration bands. In the case of the (d) comparison, the intensities were entirely different. They are given in Table III and can be seen in Fig. 3 (b).

TABLE III. *Density distribuion in high voltage discharge plates.*

Negative Bands

v' \ v''	0	1	2	3
0	15	12	8	
1	6	6	7	
2				1

Second Positive Bands

v' \ v''	0	1	2	3	4
0	15	14	10	2	
1	10	4	10	10	
2		4*		2	3

* Partially obscured by neighboring line.

Obviously this distribution has a relatively higher concentration in the lower vibrational bands than the canal-ray excitations given in Table I and II, or than in other comparison plates. It agrees quite well with Herzberg's "weak" excitation as far as the negative bands are concerned. He gives no intensities for the positive bands so comparison is not possible.

Originally we intended to study positive ion excitation and compare it with electron excitation. By this time we were pretty well convinced that we had no pure electron excitation spectra for comparison. Therefore we preceeded to get some.

ELECTRON EXCITATION

In making comparison plates with electron impact we wished to change conditions as little as possible and therefore used a tube, Fig. 4, very similar to that used for positive ions. However in order to reduce the length of exposure necessary, a filament source of electrons was used. As shown in

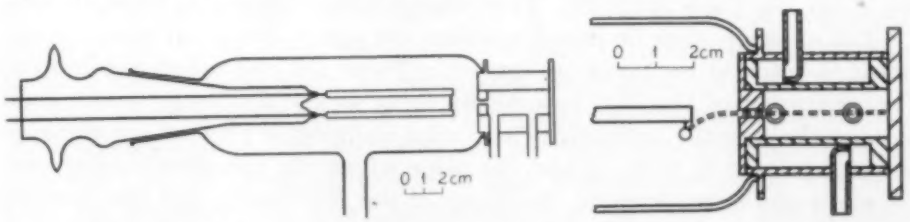

Fig. 4. (a) Schematic diagram of electron beam apparatus. (b) Details of filament, electron beam and water-cooled anode.

the figure the filament was mounted below the hole in the anode so that none of its light got into the excitation chamber. A small electromagnet was then used to bend some of the electrons into the path shown in Fig. 4. With a voltage of 700, a current to the anode of 70 milliamperes, a pressure of 0.06 mm in the excitation space and of 0.006 mm in the discharge tube a sharp luminous beam was obtained. Part of a spectrogram taken of this beam with the type E315 Quartz Hilger is given in Fig. 3(c). This was an exposure of

two hours with an Eastman Speedway plate. The estimated densities of the negative and positive bands are given below in Table IV.

TABLE IV. *Density distribution with excitation by a Beam of 700 volt electrons.*

Negative Bands

v' \ v''	0	1	2	3
0	40	25	5	—
1	8	8	7	1
2				

Second Positive Bands

v' \ v''	0	1	2	3	4
0	12	14	8	1	
1	10	1	8	7	*
2	1	1	—	—	1

Clearly we have here an extreme concentration of intensity in the low initial vibration states.

GENERAL DISCUSSION

Before making any attempt to interpret the results presented above they will be compared with previous work. First, as to the positive ray results, the photograph published by Stark and Hermann[13] shows the nitrogen canal-ray spectrum between 5500 and 3550A.U. Both the negative and positive bands are present and though the reproduction is not good enough to pick out many of the bands, there is at least no conspicuous departure from the intensity distributions of Tables I and II. A study of Fig. 4, in Fulcher's paper[10] gives a similar result. Again the reproduction given by Wilsar[14] shows the intensities of the first two sequences of the negative bands with intensities approximately like those of Table II. Doubtless a study of the original plates of these experimenters would yield really satisfactory intensity estimates. Dr. C. J. Brasefield has kindly turned over to us some early plates which he took in his work on canal rays in hydrogen[15] at a time when he was being troubled with nitrogen as an impurity. One of these plates shows eight members of the 4708 and four of the 4278 sequence of the negative bands. Their intensity is approximately as given in Table II and not at all like Table III or IV. Thus what evidence there is agrees with ours.

The question may be raised whether the excitation in all these experiments is actually by canal-ray impact. There are two other possibilities. The excitation of the N_2^+ ions might occur in the discharge before their passage through the cathode. This seems unlikely in view of the distance between the slit S_1 (Fig. 1) and the place where the spectrum is observed, the observations of Wien on the decay of the N_2^+ bands, and the pressure in the observation chamber. Or the excitation might be by secondary electrons. Considering the sharpness of the beam and the fact that it was observed nearly a centimeter beyond the last slit, this seems unlikely also.

Granted that the excitation is by canal-ray impact is the radiation observed from the canal ray or the molecule that is struck? If we are interested only in the conversion of kinetic energy of translation into energy of vibration or rotation this is not a fundamental question since it is immaterial which molecule is stationary. However, this question raises the point which was the

[13] Stark and Hermann, Phys. Zeits. **7**, 92 (1906).
[14] Wilsar, Ann. d. Physik **39**, 1251 (1912).
[15] Brasefield, Phys. Rev. **31**, 215 (1928).

chief concern of the previous papers we have been discussing, the Doppler effect. They all agree that there is no Doppler effect in the positive bands when they are observed in the canal-ray spectrum but there is not complete agreement on the negative bands. The consensus of opinion appears to be that it is either absent or very small.[11,12] In our experiments there was no sign of doubling in the bands, and as it was extremely unlikely that the shifted bands should be present without any trace of the unshifted we concluded that the Doppler effect was small or absent. But for some of the lines in the better resolved part of the spectrum there appeared to be both a shifted and an unshifted line of about the expected separation.

The conclusion is then that the intensities given in Tables I and II are confirmed by the older work and actually represent the excitation of band spectra by rapidly moving molecules of nitrogen or mercury. These molecules may or may not be charged.

Returning to the electron excitation, previous work needs to be considered. The remarkable fact is that there seems to be so little. Several authors have studied the excitation potentials of the various band systems of nitrogen[16,17,18] but of these apparently only Kneser worked with electron speeds as high as 100 volts, and made some slight study of the variation in the intensity of the different bands. His results, for both electrons of 100 volts and electrons of about 30 volts, are not very complete but as far as they go, show an intermediate intensity distribution between those of Tables I and II and those of Table III but nearer Table III. As far as one can judge from reproductions published in some of the other papers mentioned, Kneser's work is typical of the results with electron impact below 100 volts. Apparently no one has worked before with electron impact at higher voltages. Our photographs with 700 volts are a start and it is in this direction that we expect to continue our work next year.

Final Summary and Conclusion

Reviewing the whole situation we see that the parabolic intensity distribution is maintained under all types of excitation. It is presumably characteristic of the transition probabilities and therefore may be expected to be independent of excitation conditions. But the distribution along the parabola varies greatly. At one extreme with canal-ray excitation we have the intensity spread well out along the parabola toward higher quantum numbers. At the other extreme with high voltage electron excitation we have the intensity very much concentrated at the head of the parabola. This much is in accord with our original notion that the canal-ray impact may convey vibrational momentum and the electron impact may not. Intermediate types of distribution are obtained from impact of low velocity electrons and from various types of discharge. Surprisingly the electrodeless discharge supposed to be purely electronic in its excitation, gives the distribution most nearly like the canal-ray excitation. This is probably due to secondary effects which raise large numbers of the molecules into high vibration states.

[16] Turner and Samson, Phys. Rev. **34**, 747 (1929).

[17] Sponer, Zeits. f. Physik **34**, 622 (1925).

[18] Kneser, Ann. d. Physik **79**, 597 (1926) and others.

ANGLE AND ENERGY DISTRIBUTION OF ELECTRONS SCATTERED BY HELIUM, ARGON AND HYDROGEN

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Abstract

The distribution of electrons rebounding at definite angles from gaseous molecules was investigated. An electrostatic re-focussing arrangement was used to analyse the energies of the electrons. In helium, it was possible to identify the following energy losses at several angles, 21.12, 22.97, and 23.62 volts for a primary electron beam of 50 volts, but not the 19.77 and 20.55 volt losses.

The number of electrons, rebounding without loss of energy, was measured for different angles of rebound (7° to 60°) from argon, helium, and molecular hydrogen molecules, and for various energies (50 to 150 volts). A scattering curve was also obtained in helium for 100 volt electrons that had lost 21.12 volts energy. In almost all cases, the number scattered decreased rapidly as the angle increased. The higher the energy of the electrons, the more rapidly did the number fall off with increasing angle. The steepness of the curves increases as we go from argon to helium to hydrogen for the slower electrons. For the faster electrons their curves are practically superposable.

The results were compared with those of other observers and with the theoretical predictions of Mott, Mitchell and Sommerfeld.

Introduction

AN INVESTIGATION of single scattering of electrons by gaseous molecules has become a subject of particular interest, in that it enables one to appraise certain theoretical predictions of the new quantum mechanics and to verify the choice of external atomic fields used in the application of the general scattering theory.

The general theory of scattering was first investigated, from the point of view of wave mechanics, by Born.[1] Sommerfeld[2] and Mitchell,[3] using Born's general theory, have calculated the angular distribution of elastically scattered electrons in argon. Mott[4] has done the same for helium and Born[5] for atomic hydrogen. Few experimental measurements, however, have been made on the scattering of electrons by gaseous molecules. Dymond and Watson[6] have measured the distribution of inelastically and elastically scattered electrons in helium, using 210 volt electrons. Their results agreed well with the calculations of Mott. Harnwell,[7] with 120 and 180 volt electrons, has measured the scattering in atomic and molecular hydrogen. Arnot[8]

[1] M. Born, Zeits. f. Physik **38**, 803 (1926).
[2] Atombau und Spektrallinien Wellenmechanischer Ergänzungsband, p. 226.
[3] A. C. G. Mitchell, Nat. Acad. Sci. Proc. **15**, 520 (1929).
[4] N. F. Mott, Proc. Cam. Phil. Soc., **25**, 304 (1929).
[5] M. Born, Gottingen, Nachr. p. 146 (1929).
[6] Dymond and Watson, Proc. Roy. Soc. **125A**, 660 (1929).
[7] G. P. Harnwell, Phys. Rev. **34**, 661 (1929).
[8] F. L. Arnot, Proc. Roy. Soc. **125A**, 660 (1929).

obtained scattering curves for 80 volt electrons in mercury vapor. Little work has been done, however, using a large range of velocities in conjunction with several scattering gases.

It was the purpose of this investigation to measure and compare the angular distribution of electrons elastically scattered by the three gases, helium, argon and molecular hydrogen, when colliding electrons of several energies are used. The energies used were 50, 75, 100 and 150 volts. The angles investigated ranged from 7° to 60°. The distribution of inelastically scattered electrons in helium was likewise determined for 100 volt electrons. This investigation also includes a measurement of the energy losses in helium at various angles.

Description of Apparatus

The apparatus used in this investigation may be briefly described as consisting of an electron projector A, a collision chamber B and an analysing chamber C. A diagram is given in Fig. 1. Electrons leaving the projector A were scattered by the gas molecules in chamber B. After single collisions in B the electrons passed through the slit s_4 into the analyser C. The two cylindrical plates, M and N in C, when set at the correct potentials, deflected the electrons into the Faraday cylinder F.

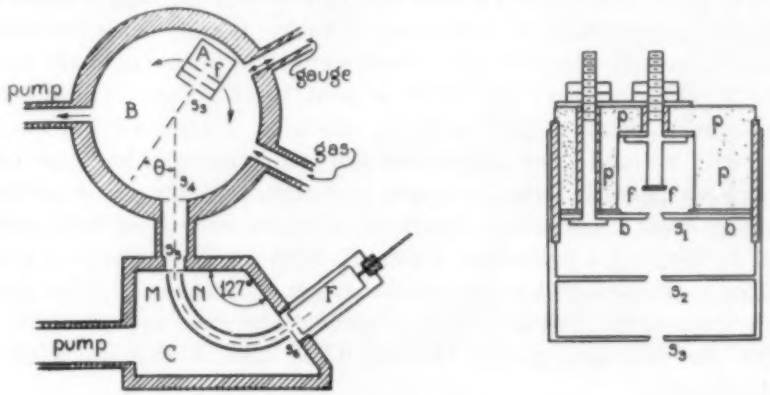

Fig. 1. Diagram of apparatus.

The projector, as shown in Fig. 1, consisted of an oxide coated filament f, a grid b with slit s_1, a final grid with the two slits, s_2 and s_3, and a back plate p. All parts were made of brass, with the exception of the plate p, which was constructed of aluminum alloy. A glass cylinder and mica sheets were used as insulators. The potential on the final double slits, s_2 and s_3, determined the energy of the electrons projected through the slit. The potentials on b and p were fixed so as to give the maximum emission from the projector, or gun, as it is sometimes called. The slits of the gun play an important part, since they are the chief source of slow electrons. Their lips were sharply bevelled and sooted to eliminate slit-scattering. The dimensions of the slits were $s_1 = 1$ mm $\times 15$ mm, $s_2 = 0.8$ mm $\times 14$ mm, $s_3 = 0.4$mm $\times 14$ mm.

The projector could be rotated about the axis of the cylindrical chamber B. In B the electrons collided with the gaseous molecules and were reflected

at various angles. Only those electrons which were reflected at an angle θ entered the analysing chamber. This angle was determined by the gun-setting. The gun was fastened to a brass tube which fitted into a ground glass joint. The ground glass joint was waxed into the back end of the brass chamber B. On to the front end was fastened a thick glass plate. A copper screen placed on the inside surface of the glass plate insured the equipotentiality of chamber B.

The analysing chamber was connected to the collision chamber B by a short brass tube. The two chambers were separated by two slits; s_4, 2mm $\times$14mm and s_5, 0.3mm$\times$10mm. The angle subtended at s_5 by s_4 measured one and a half degrees. The cylindrical plates M and N were bolted to the wall of the chamber and insulated from it by sheets of mica. The radii of curvature of the plates were 50 mm and 60 mm respectively. The plates formed an arc which subtended an angle of 127° 17′. It has been shown, and predicted by theory, that the potential difference between the plates necessary to deflect electrons from s_5 to s_6 is proportional to the energy of the electrons The particular chamber and the properties of the electrostatic analysing method have been described by Hughes and Rojansky[9] and Hughes and McMillen.[10] The Faraday cylinder was connected to a Compton electrometer.

The gas to be investigated flowed into chamber B through a small capillary and was pumped out by a mercury diffusion pump. This arrangement maintained a steady pressure and a fresh supply of pure gas in the collision chamber B. The pressure was read on a McLeod gauge. To secure high pumping speeds, a glass tube of large diameter connected the analysing chamber with a Gaede two stage steel diffusion pump. The gases used in this experiment were helium, hydrogen and argon. Helium was purified by slow passage over charcoal at liquid air temperature. The hydrogen was obtained by heating a palladium tube. A discharge in the presence of calcium vapor was employed to purify the argon. To freeze out the mercury liquid air traps were inserted. The following pressures in mm of Hg were used with the following gases: helium, 0.008 mm; hydrogen, 0.006 mm; argon, 0.004 mm.

Energy Losses in Helium

To measure the energy losses, the projector was set at some fixed angle and the electron current to the Faraday cylinder noted for each set of potentials on the deflecting plates. The energy of the deflected electron is readily obtained from the potential on the deflecting plates when the ratio of the energy of the deflected electron to the deflecting potential is known. This ratio was established when no gas was in the apparatus. One can then obtain a set of curves plotting the number of electrons against their energy. Unfortunately, because of excess scattering of the slits and other unaccounted for defects in the apparatus, the original curves had to be modified by subtracting from them spurious peaks and background scattering which were also present in the absence of any gas.

[9] Hughes and Rojansky, Phys. Rev. **34**, 284 (1929).
[10] Hughes and McMillen, Phys. Rev. **34**, 291 (1929).

In Fig. 2 can be seen an energy loss curve for helium. This curve was taken with electrons of 50 volts energy and indicates the energy losses for those deflected at 10°. The abscissa measures the energy of the electrons after collision, while the ordinate measures the number of electrons having that particular energy. The energy loss is also indicated in the diagram. The main peak at 50 volts, comprised of electrons making elastic impacts, is many times higher than the remaining peaks and extends off the figure. A group of peaks is seen near 30 volts energy region, indicating losses of the order of 20 volts. In this group there are three distinguishable peaks. The obvious lack of symmetry of the main energy-loss peak suggests a smaller peak, or peaks, overlapped by the main peak. One notes, too, on the low

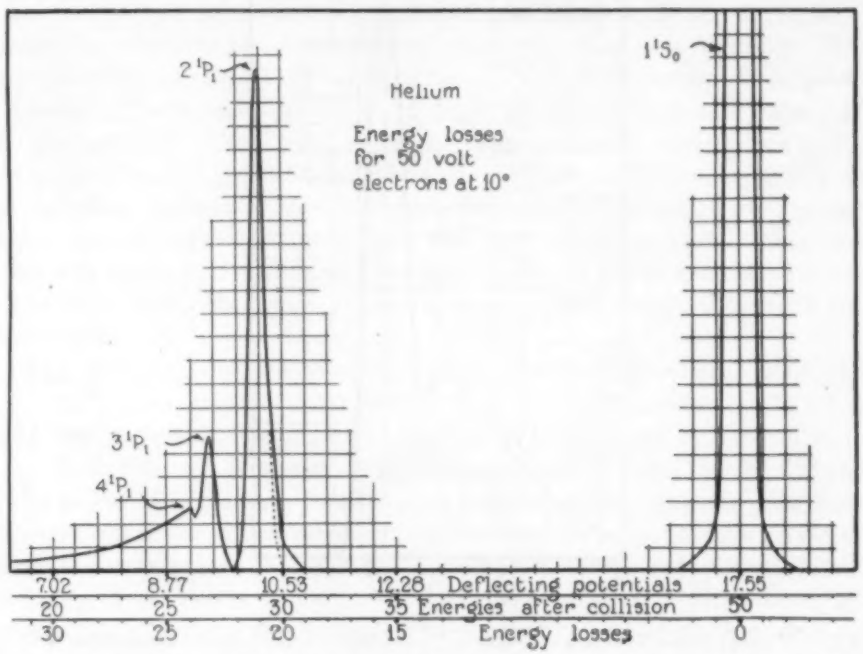

Fig. 2. Energy losses in helium for 50 volt electrons simultaneously deflected at 10°.

energy side of the last peak, that there is a gradual shading off in intensity. Fig. 3 shows the main energy-loss peak and the composite subsidiary peak for 100 volt electrons. For the case of electrons of 100 volts energy the lesser peaks have become indistinguishable because of the poor resolving power at higher voltages. These curves are similar to those obtained by Dymond,[11] who used the magnetic deflection method.

In identifying these energy-loss peaks great care was taken in measuring the magnitude of the energy loss of the main energy-loss peak, and the remaining peaks were then referred to it. The procedure was carried out in the following way: the main beam of electrons was directed into the gas at a definite energy, as read on the accelerating voltmeter. With the deflecting potential set at the value to give the main energy-loss peak, the energy of the

[11] E. G. Dymond, Phys. Rev., **29**, 433 (1927).

original beam was lowered until the main beam reached an energy value such as to be directed into the Faraday cylinder. The reading of the voltmeter under those conditions subtracted from the original setting read directly the energy loss in volts. This method of measurement demanded only two readings and both readings were taken on the same voltmeter, thus giving greater accuracy. Also the difference read in this manner was three times the corresponding unconverted reading on the deflecting potential voltmeters.

A set of 15 readings over a range of 50 to 150 volts gave for the main energy-loss peak an average energy loss value of 21.50 with the probable

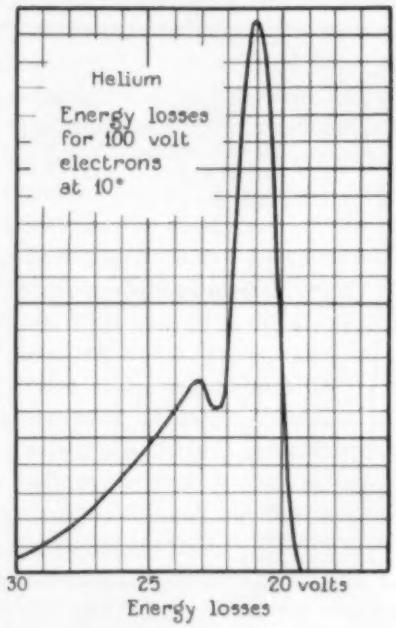

Fig. 3. Energy losses in helium for 100 volt electrons simultaneously deflected at 10°.

error of 0.15 volts. One has from spectroscopic data the following possible energy losses: 19.77, 20.55, 21.12, 22.98, 23.63, etc., corresponding to the transitions $1^1S_0-2^3S_1$, $1^1S_0-2^1S_0$, $1^1S_0-2^1P_1$, $1^1S_0-3^1P_1$ and $1^1S_0-4^1P_1$ respectively. The above measured-loss 21.5 lies closer to the spectroscopic value 21.12 than to any of the others, which indicates that the main energy loss peak corresponds to the 21.12 loss or to the first transition in the principal series, $1^1S_0-2^1P_1$. This choice is further supported by a series of measurements taken on the other two peaks. These measurements were taken directly from the energy-loss curves and measured as separations of the two small peaks from the main energy-loss peak. These measured separations of the two small peaks from the main energy-loss peaks showed that in matching experimental separations of energy losses with the various combinations of possible separations taken from spectroscopic data a good match was obtained by assigning to the main energy-loss peak the transition

$1^1S_0-2^1P_1$, as was done above, and to the next two peaks the transitions $1^1S_0-3^1P_1$ and $1^1S_0-4^1P_1$ respectively. The averaged separation between the first main peak and the next was 2.13, while the spectroscopic difference between 2^1P_1 and 3^1P_1 is 1.85. The averaged experimental separation between the two lesser peaks is 0.82, and the spectroscopic difference between 3^1P_1 and 4^1P_1 is 0.65. This is fairly good agreement, in view of the uncertainty of measurement for the low intensity peaks. Dymond, in his paper on electron scattering, attributed the main energy-loss peak to the 20.55 loss, which, in view of the above results, seems to be untenable. Further support for the identification of this main energy-loss peak as the 21.12 loss peak is obtained from probability considerations. Attributing the main energy-loss peak to the transition associated with the 21.12 loss indicates, in view of the prominence of this peak, that this loss is by far the most probable in the 50 volt energy range. This is in accord with the work of Glockler,[12] who measured double impact losses in helium by the partial current method. Glockler's most prominent double impact peak, 40.86, was assigned to the transitions 21.12 and 19.77, the 21.12 loss occurring when the colliding electron had 40.86 volts energy. Dymond,[13] also using the double impact method, found that the most probable loss in this energy range was 20.9 ± 0.2, which, in view of the present work, should be assigned to the 21.12 loss. However, Dymond assigned this energy difference to the 20.55 transition.

The indication of one or more peaks on the high energy side of the $1^1S_0-2^1P_0$ peak is in such a position as to be due to either a 19.77 loss, a 20.55 loss, or both. The gradual tapering off in intensity evident after peak *C* can be explained, as was done by Dymond and Watson, as the composite of the peaks of decreasing intensity corresponding to the remaining lines in the principal series. It is interesting to note that no peak appears corresponding to the energy lost in ionization, i.e. at 24.5 volts. In the first place, the efficiency of ionization is low for 50 volt electrons and, in the second place, there are now two electrons after collision, and conceivably, they may share the excess energy in all possible combinations.

The energy-loss values showed no variation when measurements were made for various angles The angles used ranged from 0° to 20°. It was also observed that there were no variations in the energy-loss values outside of the experimental errors of the apparatus when colliding electrons of energies ranging from 40 to 150 volts were used.

Angular Distribution of Rebounding Electrons

The angular distribution curves for electrons making elastic impact were determined for the two monatomic gases, helium and argon, and the diatomic gas hydrogen. The energies of the colliding electrons ranged from 50 volts to 150 volts, while the angles investigated extended from 7° to 60°. An inelastic scattering curve was also obtained for helium with electrons of

[12] G. Glockler, Phys. Rev. **27**, 423 (1926).
[13] E. G. Dymond, Proc. Roy. Soc. **107A**, 291 (1925).

100 volts. These curves have been plotted so as to indicate the proportionate number of electrons scattered per unit solid angle at the angle indicated. The abscissa is calibrated in degrees, while the ordinate is graduated in

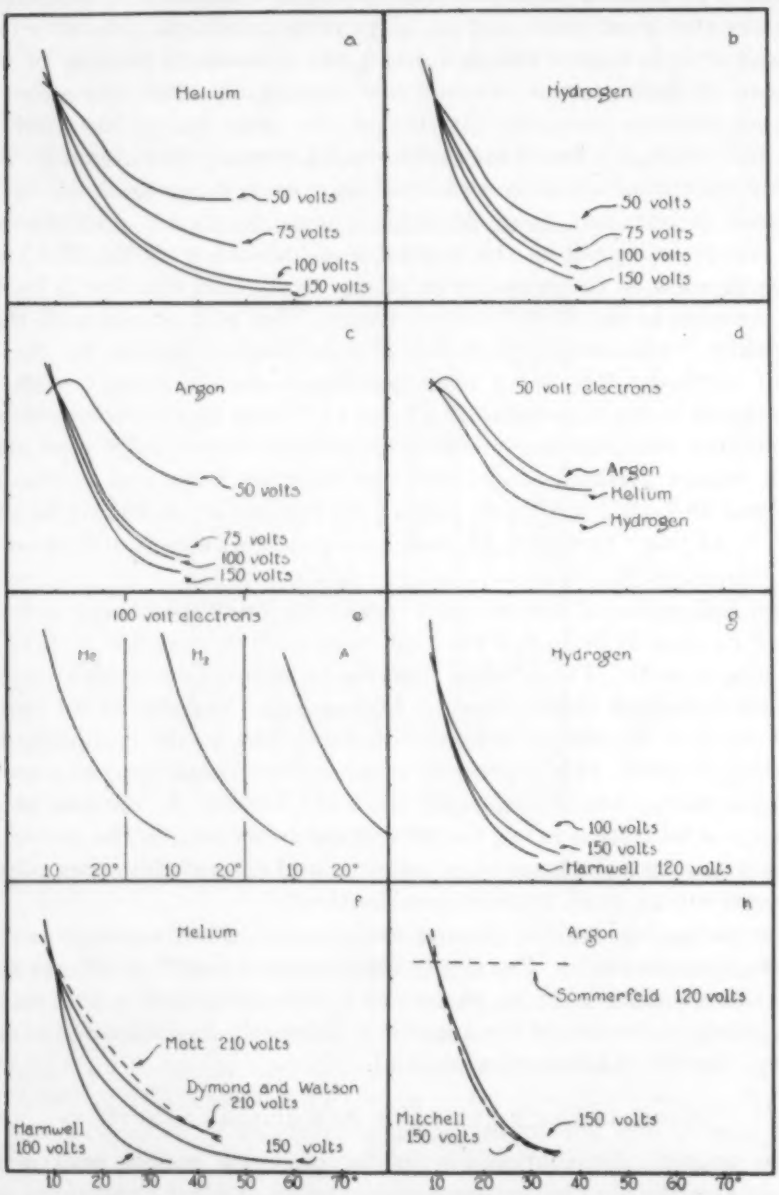

Fig. 4. Distribution per unit solid angle of elastically scattered electrons.

arbitrary numbers. All curves given in the accompanying figures were so arranged as to coincide at 10°. This was a necessary procedure because of the difficulty one encounters in attempting to measure the absolute value of the intensity of the scattered electrons.

A scattering curve was obtained by setting the potentials on the deflecting plates in the analyser to correspond to one of the peaks of the energy-loss curve and by measuring the electron current to the Faraday cylinder for various settings of the projector. The total number scattered upon a collision with an energy-transfer or upon elastic collision at any angle is proportional to the area under the corresponding peak of the energy-loss curve taken at that angle. A separate investigation showed that the area under the peak was proportional to its height, which justifies the procedure of taking the height of the peak as a measure of the number scattered at that angle. There were always present in the scattering curves some spurious electrons. In order to correct for these, their magnitude was determined by a separate set of readings with no gas in the apparatus and subtracted from the original curve. The magnitude of this spurious curve was much greater, however, than its effective magnitude when the gas was present. This was due to the fact that the electrons causing the spurious peaks were partially absorbed or scattered by the gas molecules as they pass from the gun slit to the analysing chamber slit. Hence the spurious curve obtained with no gas in the apparatus was reduced before being subtracted from the original curve. A further correction had to be applied to the original scattering curve in order to correct for the variation of scattering volume with changes in the angle of the projector. It is apparent that the collision volume, the volume common to the emission wedge from the projector and the reception wedge of the slit s_3, varies as $1/\sin\theta$. To reduce, then, one's readings to the same volume of collision, one multiplies the results by the $\sin\theta$.

The angle θ was measured accurately by a protractor and pointer arranged outside the apparatus. Because of the fact that the gun emitted a wedge-shaped beam of electrons, some electrons were measured after having been deflected at an angle other than that of θ. This discrepancy in the value of θ became appreciable only for small values of θ The co-latitude angle measured in the plane perpendicular to the paper in Fig. 1 remains the same for all settings of the projector. Its magnitude is approximately equal to the length of the slit-entrance of the Faraday cylinder divided by the path from the gun to the Faraday cylinder. It is about 2°.

The elastic scattering curves, i.e., curves indicating the angular distribution of electrons rebounding from elastic collisions, can be advantageously studied, by comparing curves for one gas with electrons of various energies and then by comparing the curves for the various gases with colliding electrons of the same energy. The three sets of curves taken with the three gases, helium, argon and hydrogen, are shown in the accompanying figure; helium, Fig. 4(a); hydrogen, Fig. 4(b); argon, Fig. 4(c). An inspection of these curves shows the following characteristics:

(a) First, one observes that the curves for electrons of lower energy are much less steep than those of higher energy. That is to say, the higher the energy of the electrons, the less the deviation from the undeflected path. This is true for all three of the gases used.

(b) It can also be seen that the change in slope of these curves is more

evident in the comparison of the 100 volt and 50 volt curves than in the comparison of the 100 volt and 150 volt curves. Thus, the change in slope with energy of the colliding electron is more marked at low velocities.

(c) One further notes a change in shape of the low energy curves. These curves flatten out at small angles, indicating a smooth hump in this small angle region. The higher energy curves, on the other hand, rise steeply with no suggestion of becoming horizontal. The argon curve for 50 volts, Fig. 4(b), has a definite hump at 12°.

(d) In Fig. 4(d) are superimposed the 50 volt curves of the three gases, helium, hydrogen and argon. The curves are very different, argon showing a much greater degree of scattering than helium and helium a greater degree than hydrogen.

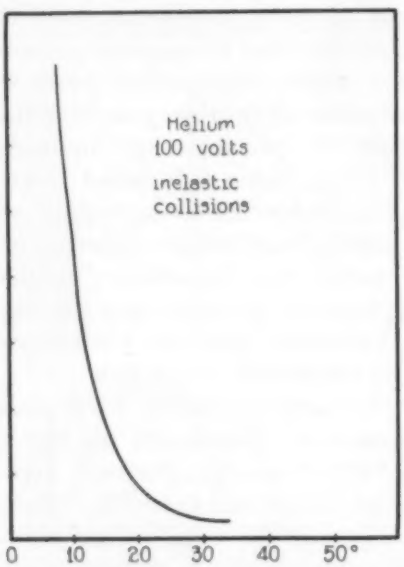

Fig. 5. Distribution per unit solid angle of electrons scattered from helium molecules with a loss of energy corresponding to the transition $1^1S_0-2^1P_1$.

(e) For electrons of greater energy, energies of 100 or 150 volts, the curves for the three gases do not differ much. An inspection of Fig. 4(e) shows that there is very little difference between the three curves when the 100 volt electrons were used. The change in slope, then, for various gases is only evident with electrons of low energy.

It was also possible to obtain an angular distribution curve for electrons having lost energy upon collision. In Fig. 5 is shown the distribution for electrons having lost energies corresponding to the $1^1S_0-2^1P_1$ transition in helium. The curve drops off rapidly, showing that electrons losing energy are only slightly deflected by the collision. Dymond and Watson's inelastic curve is in agreement with the one obtained in this investigation.

Discussion of Scattering Measurements

Although these scattering curves allow certain definite observations to be made concerning the behavior of scattered electrons when the scattering

gas is varied and when the energy of the colliding electrons is varied, no simple collision process, such as that used most successfully by Rutherford in his theory of α-ray scattering, based on classical methods, is forthcoming. A collision theory based upon the new mechanics, however, has been developed by Born. All collision theories make this one observation; namely, the decrease in the degree of scattering for electrons of higher energy, an observation in accord with the results obtained in this investigation.

For helium Mott has applied this general theory to elastic collisions, assuming an atomic force field given by Hartree's selfconsistent fields. The result, however, applies to relatively fast electrons and has only been worked out for 210 volt electrons. An experimental curve for scattering in helium has been obtained by Dymond and Watson for 210 volt electrons which agrees well with Mott's theoretical curve, but which is less steep than our 150 volt curve, as can be seen in Fig. 4(f). This difference between the results of Dymond and Watson for 210 volt electrons and our results for 150 volt electrons is of too great a magnitude and in the wrong direction to be explained as a difference caused by the use of two different electron velocities. Harnwell, in a qualitative investigation of helium,observed very little difference in the degree of scattering by helium and by hydrogen (an observation verified in this investigation for high velocity electrons). If this is so, Harnwell's hydrogen curve may be used as an estimate of his helium scattering curve. Investigation of Fig. 4(f) shows that this curve is much steeper than either Dymond and Watson's or the author's. These three measurements of elastic scattering in helium, although at variance with each other, are all much closer to the prediction of Mott, based on the new mechanics, than to the results obtained when one assumes the Coulomb field.

In Fig. 4(g) can be seen Harnwell's 120 volt hydrogen curve and the 100 and 150 volt hydrogen curve as obtained in this investigation. (Harnwell's curve has been replotted from the original data to indicate the number scattered per unit solid angle at the angle θ. The original data was given as the number scattered in the total solid angle subtended between θ and $\theta+\Delta\theta$). Harnwell's curve is much steeper than either our 100 or 150 volt curve. It is difficult to explain this discrepancy. No theoretical results have been given for molecular hydrogen.

Both Mitchell and Sommerfeld have calculated the degree of scattering for argon. Sommerfeld has applied Born's general collision theory and obtained an atomic force field by assuming that all the electrons were situated in the K shell. For 120 volt electrons Sommerfeld finds practically no change in the number of electrons scattered as the angle is increased from 0° to 90°. This does not agree with the results obtained above. Mitchell has adopted an atomic field force given by Fermi and calculated the degree of scattering in argon for electrons of various velocities. Fig. 4(h) shows good agreement for the 150 volt electrons. The figure also gives Sommerfeld's results approximately. Mitchell's curves for the lower velocities did not agree well with our experimental values. (Dr. Mitchell very kindly contributed the data, as yet unpublished, used in drawing the above curve.)

In conclusion I wish to thank Professor A. L. Hughes, under whose direction this work was carried out.

THE INTENSITY OF X-RAY SATELLITES*

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Cornell University and Bureau of Standards

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Abstract

By means of the two-crystal ionization spectrometer measurements have been made of the wavelengths and intensities relative to $K\alpha_1$ of the satellites $K\alpha_{3,4}$ of Cu (29). $K\alpha_{3,4}$ has characteristics of a doublet and is separated, photographically, for elements below Sc(21) but is unresolved for elements of higher atomic number. The greater resolving power of the two-crystal spectrometer shows that this "doublet" contains, probably, more than the two components $K\alpha_3$ and $K\alpha_4$, the wavelengths of which latter were found, respectively, to be 1531.15 and 1530.15 X.U. The intensity of either of these components, at 40 K.V., is of the order of 0.25 percent of the intensity of $K\alpha_1$. A similar study of the $K\alpha_{3,4}$ doublet of Ni (28) suggests that this doublet may contain four components.

IT IS generally agreed that x-ray satellites have their origin in "doubly ionized atoms[1] for which reason these lines are sometimes called "spark lines." A knowledge of the intensities of the satellites relative to each other and to the intensities of the respective parent lines should therefore provide a basis for estimating the relative probabilities of single and double ionization in the target of the x-ray tube. Such information would materially assist in clarifying the present theories regarding the origin of these lines.

Up to the present only the roughest estimates of the intensities of satellites have been made. Practically all studies of satellites have been made by the photographic method. To bring out the satellites on a photographic plate requires that the parent lines should, usually, be very much over-exposed, so that direct comparison of intensities is difficult. Further, many of the satellites lie "in the shadow" of the parent line, the shape of which, were there no satellites, must be estimated (guessed!) in order to make even a semiquantitative determination of relative intensity.

According to such estimates as are available the relative intensities of satellites vary from a small fraction of one percent to several percent of the intensities of the respective parent lines. The several satellites of a given line vary among themselves. For example, the $K\alpha$ doublet has several satellites of which the doublet $K\alpha_{3,4}$ is much more intense than $K\alpha_{5,6}$. $K\alpha_4$ is more intense, perhaps by a factor of two, than $K\alpha_3$, for elements in the neighborhood of $Z=20$. But for Si(14) and below, $K\alpha_3$ is the more intense. The $L\alpha$ doublet, likewise, has several satellites[2], $L\alpha^{i}$, $L\alpha^{ii}$, $L\alpha^{iii}$ $\cdots$ $L\alpha^{vi}$ in order of

* For preliminary report see Science **70**, 616 (Dec. 20, 1929).

** The senior author wishes to express his thanks to the Heckscher Research Council of Cornell University for a grant in aid of this research.

[1] For a discussion of x-ray satellites and their origin see M. J. Druyvesteyn, Dissertation, Groningen, 1928. F. K. Richtmyer, Franklin Inst. Journal **208**, 337ff (1929).

[2] For terminology see F. K. Richtmyer, Jour. Franklin Inst., reference 1.

decreasing wave-length. Of these $L\alpha''$ and $L\alpha'''$ are the most intense. $L\alpha^{v}$ and $L\alpha^{vi}$ are very faint.

The relative intensities vary, for any given satellite, with atomic number. The $K\alpha_{3,4}$ doublet is relatively strong for $Z=20$; it is very faint for $Z=30$ and practically disappears for $Z=33$. $K\alpha_{5,6}$ is easily observed from Na(11) to Si(14) but disappears above S(16).

It is also probable, since the excitation voltages of satellites are somewhat higher than those of the parent lines, that the law of increase of intensity with voltage differs from the corresponding law for the parent line, and hence, at least for voltages not too far above the excitation voltage, that the intensity of a satellite relative to parent line depends, for a given element, on the voltage.

The present investigation was undertaken to obtain information which might serve as a starting point for a systematic study of this general problem. The $K\alpha_{3,4}$ doublet of Cu(29), a (photographically unresolved) satellite of the $K\alpha_{1,2}$ doublet, was chosen as most suitable for an initial study. An x-ray tube with a copper target can be built to stand, with water cooling, an input of at least 2500 watts. And Davis and Slack have developed a window thin enough to transmit to the outside of the x-ray tube, a substantial proportion of Cu$K\alpha$ radiation so that it may be studied by an ionization spectrometer. The two-crystal x-ray spectrometer developed by Bergen Davis[3] and his collaborators is particularly suited for this purpose, partly because of its high resolving power and partly because of the intense beam of monochromatic radiation which it delivers.

With the two-crystal spectrometer and water-cooled, copper-target tube with thin window, observations were made of the apparent energy distribution through the line Cu$K\alpha_1$ and to a considerable distance toward shorter wave-lengths. The method of making observations requires no special comment, save only that every effort was made to maintain conditions constant during a run, by manually controlling voltage and tube current. The x-ray tube was run at approximately 40 kv and 50 ma.

The results are best shown by Fig. 1 which is the average of several runs. The abscissae represent Bragg reflection angles in seconds (starting from an arbitrary zero). The ordinate scale A gives the intensity distribution through the line $K\alpha_1$. The measurements below 300″ are plotted to ordinate scale B. A distinct "hump" is observed to extend from about 60″ to 200″. The observed points above and below this "hump" define a smooth line, abc. If the ordinates of this line be subtracted from the observations and these differences plotted on the abscissae scale there results the line pqr, which is the $K\alpha_{3,4}$ satellite of Cu(29). Photographic determination (by Siegbahn) of $K\alpha_{3,4}$ places the doublet (unresolved on the photographic plate) at 150″ as shown at "C" on the abscissae scale.

[3] A substantial proportion of the work herein described was done in the Physical Laboratory at Columbia University with the double x-ray spectrometer, x-ray plant and accessory equipment previously assembled by Professor Bergen Davis. To him and his colleagues, particularly Mr. Beller, the authors wish to express sincere thanks not only for the use of the apparatus, including the specially constructed x-ray tube, but for many other courtesies and suggestions during the progress of the work.

It is obvious that $K\alpha_{3,4}$ as here observed by the ionization spectrometer is at least a doublet, as Siegbahn found it to be by the photographic method for elements of atomic number below Sc(21). For, not only does the line have the appearance of a close doublet in spite of some scattering of the points, but, as shown on Fig. 1, the width at half-maximum of $K\alpha_1$ is 28 seconds of arc, while the corresponding width of $K\alpha_{3,4}$ is 83″. This suggests that $K\alpha_{3,4}$ may contain several components. The resolution is not sufficient to warrant an attempt accurately to determine these components. If, however, starting from the long-wave-length side, a line $rq'p'$, Fig. 1, be constructed with the same width at half-maximum as $K\alpha_1$, the long-wave-length component of $K\alpha_{3,4}$ can be approximately located. This long-wave-length component,

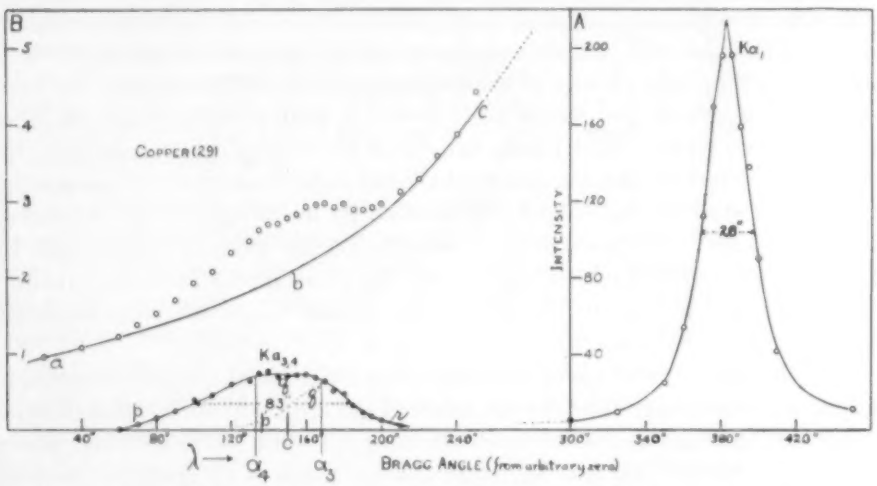

Fig. 1. Energy distribution through $K\alpha_1$ of Cu(29) including its satellites $K\alpha_{3,4}$. The abscissa scale represents Bragg reflection angles, in seconds, from an arbitrary zero. (The actual Bragg angle for Cu $K\alpha_1$ (calcite) is about 14°42′). Ordinate scale A gives the distribution through $K\alpha_1$. Ordinate scale B applies to the short wave-length "foot" of $K\alpha_1$ as shown by the line abc. The satellite doublet, $K\alpha_{3,4}$, shown by the line pqr, is the difference between the smooth line abc and the corresponding observed points. Two of the components of $K\alpha_{3,4}$ are estimated to be at "α_3" and "α_4", respectively, The photographic method locates the doublet at "C".

i.e. $K\alpha_3$, is thus located at "α_3" on the graph. Taking the maximum ordinate of the remainder as the next component, we locate $K\alpha_4$ at "α_4" on the graph. We are then able to compute the wave-lengths of $K\alpha_3$ and $K\alpha_4$ as follows:

	$K\alpha_3$	$K\alpha_4$
$\Delta\theta$ from $K\alpha_1$	217″	252″
λ from $K\alpha_1$	6.15 $X.U$	7.15 $X.U.$
λ ($\lambda K\alpha_1$ = 1537.30 $X.U.$)	1531.15″	1530.15″
$\Delta\nu/R$ from $K\alpha_2$	3.85	4.23
$(\Delta\nu/R)^{1/2}$ from $K\alpha_2$	1.96	2.06

Siegbahn gives 1530.7XU. as the wave-length of the (photographically unresolved) doublet $K\alpha_{3,4}$ of Cu (29). The mean of the wave-lengths given above is 1530.65XU.

One of us[4] has shown that a simple relation exists between the frequency ν of a satellite and that of the corresponding parent line; namely, $(\Delta\nu/R)^{1/2}$ is a linear function of atomic number, where R is the Rydberg constant and $\Delta\nu$ is the difference in frequency between the satellite and the parent line. For the $K\alpha_{3,4}$ satellites it was found that this linear relation held if $\Delta\nu$ was taken as the difference in frequency between $K\alpha_3$ or $K\alpha_4$ and the parent line $K\alpha_2$ (instead of $K\alpha_1$). The graph of this relation is shown in Fig. 2. The data for

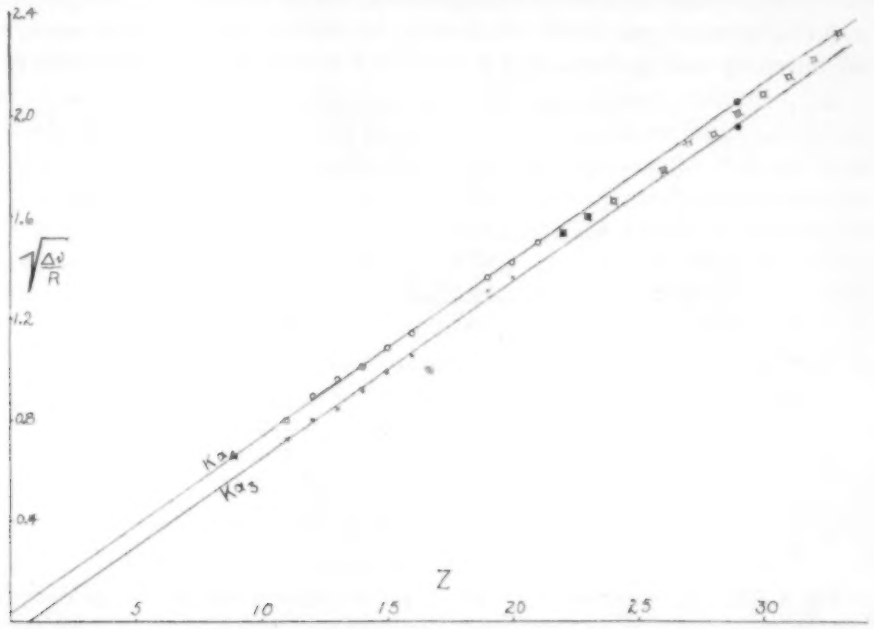

Fig. 2. The square root of the difference in frequency between a satellite and its parent line is a linear function of atomic number. Upper line: Square root of difference in frequency between $K\alpha_1$ and $K\alpha_2$; lower line, same for $K\alpha_3$. Source of data: Na(11) to Ni(28) from Siegbahn; Cu(29) to As(33) from F. K. R. at Cornell University). The solid circles are the present measurements for Cu(29) by the two-crystal ionization spectrometer.

the elements Na(11) to Ni(28) are taken from Siegbahn. Below Ca(20) the two components are resolved and are shown, respectively, by circles (for $K\alpha_4$) and crosses (for $K\alpha_3$). From Sc(21) to Ni(28) the "circle-cross" represents the unresolved doublet. The last five points (circle-cross), namely Cu(29) to As(33) are from unpublished data taken by one of us (F.K.R. at Cornell University). It is seen that these unresolved points fall between the two parallel lines defined by the elements, below Ca(20), for which the doublet is resolved.

[4] F. K. Richtmyer, Phil. Mag. **6**, 64 (July, 1928); Franklin Inst., Jour. **208**, 325 (Sept., (1929). Also F. K. Richtmyer and R. D. Richtmyer, Phys. Rev. **34**, 574 (1929)

The two solid circles at Cu(29) represent the doublet as resolved by the two-crystal spectrometer (See above data table). The closeness with which these two points fall on the respective lines seems to justify the conclusion that the difference in $(\Delta\nu/R)^{1/2}$ is constant and independent of atomic number, which empirical fact forms a basis for the term "doublet" as applied to $K\alpha_{3,4}$.

Referring now to Fig. 1 the maximum ordinate of $K\alpha_{3,4}$ is about 0.72; that of $K\alpha_1$ is about 215. The intensity of the components of $K\alpha_{3,4}$ is not greater than $0.72/215 = 0.0034$ of that of $K\alpha_1$, and in reality is somewhat less, since the line *pqr* has a higher maximum than any of its components. In round numbers, therefore, we may say that $K\alpha_1$ is some 400 times as intense as the $K\alpha_{3,4}$ satellites for the element Cu(29) at 40 kv.

A similar study was made of the $K\alpha_{3,4}$ of Ni(28). The results of two runs at two different voltages are shown at *A* and *B* of Fig. 3. The satellites are

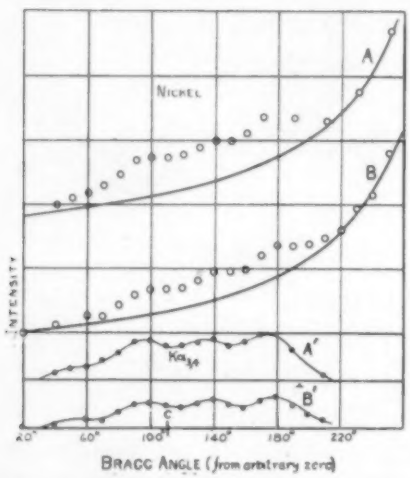

Fig. 3. The $K\alpha_{3,4}$ satellites of Ni(28). *A* and *B* represent observed energy distribution along the foot of $K\alpha_1$ of Ni, for two different tube voltages; *A'* and *B'*, the corresponding energy distribution through the satellites. The photographic method places the (unresolved) satellite at "*C*".

are shown at *A'* and *B'*. Photographic measurement places the doublet at "*C*." Further measurements are necessary to determine whether $K\alpha_{3,4}$ for Ni actually has three (or perhaps four) components as these data seem to indicate. Unpublished data[5] at Cornell University show that $K\alpha_3$ splits up into two components for elements below S(16).

No determination of the intensity of $K\alpha_{3,4}$ for Ni(28) relative to $K\alpha_{1,2}$ has been made since, as may be observed from Fig. 3, the absence of observations on the short-wave-length side makes it impossible to locate the base line accurately. However, the order of magnitude of relative intensity is the same as for Cu(29).

Since $K\alpha_1$ and $K\alpha_2$ originate from the same initial ionized state, namely single *K*-ionization, we may, by analogy, assume that the components of

[5] By O. Rex Ford.

$K\alpha_{3,4}$ originate in the same double ionized state which we may for the present call a KX-ionization, "X" standing for a missing electron the identity of which is as yet undetermined. Let P_K and P_{KX} be the relative probabilities of these single and double ionizations, respectively, under any given set of conditions—tube current, voltage, etc. Then, these data on relative intensities of one of the components of $K\alpha_{3,4}$ to $K\alpha_1$ make possible the estimate that (for Cu(29) at about 40 kv).

$$P_{KX}/P_K \geqq 1/400.$$

This estimate, of course, is very rough and gives only the order of magnitude of the ratio, as may be seen from the following: A K-ionized atom may return to the normal state by various routes. As a first step, it may emit any one of the diagram lines of the K series; or, as a result of autophotoelectric absorption, it may emit a photoelectron. We may expect, likewise, that a KX-ionized atom might return to the normal state in various ways other than by the emission of $K\alpha_{3,4}$. Indeed, there is some evidence[6] to indicate that, associated with some, at least, of the satellites, there is a continuous spectrum which may account for a considerable proportion of the doubly ionized atoms. The asymmetry of the satellite curves in Figs. 1 and 3—i.e., these curves are less steep on the short wavelength side—is suggestive of a continuous spectrum similar to that found with $L\alpha$ satellites in Fig. 1 of the article just cited[6].

It is hoped later to make a more extensive report on relative intensities of satellites on the basis of work now in progress at Cornell University.

[6] F. K. Richtmyer and R. D. Richtmyer, Phys. Rev., reference 4.

AN ANALYSIS OF SCATTERED X-RAYS WITH THE DOUBLE CRYSTAL SPECTROMETER

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(Received August 7, 1930)

Abstract

X-rays from a molybdenum target were scattered by graphite at approximately 109° and 161°. The scattered rays were analyzed with a double crystal spectrometer. When scattering at 109° was used, no indication of the fine structure lines, reported by Davis and his collaborators, could be found. When scattering at 161° was used, the modified $K\alpha_1$ and $K\alpha_2$ lines were definitely separated. The value of $\delta\lambda$ was 0.04721 $\pm$0.00003A, the value of $(1-\cos\phi)$ was 1.9479 and the calculated value of h/mc was 0.02424 $\pm$0.00004A.

Introduction

When monochromatic x-rays are scattered by matter, both their intensity and their wave-length are changed. A theory explaining their change in wave-length was suggested by A. H. Compton,[1] in 1922. This theory assumed that x-rays were scattered by free electrons and gave the equation,

$$\delta\lambda = (h/mc)(1 - \cos\phi) \tag{1}$$

for their change in wave-length. In the above equation, $\delta\lambda$ represents the change in wave-length; h, Planck's constant; m, the mass of an electron; c, the velocity of light; and, ϕ the angle of scattering. The change in wave-length has been measured by many investigators,[2] and their results have for the most part agreed very well with the theory. In 1924, A. H. Compton[3] proposed a theory for the scattering of x-rays by bound electrons. The energy equation for this type of scattering is

$$h\nu = h\nu' + h\nu_s + mc^2\left[(1 - \beta^2)^{-1/2} - 1\right] + \tfrac{1}{2}MV^2 \tag{2}$$

where h is Planck's constant, ν the frequency of the incident x-rays, ν' the frequency of the scattered x-rays, ν_s the characteristic frequency of the s^{th} level in the atom, $mc^2\left[(1-\beta^2)^{-\frac{1}{2}}-1\right]$ the kinetic energy of the recoil electron, and $1/2\ MV^2$ the kinetic energy given to the atom of mass M. The kinetic energy given to the atom is negligible, so that only the first three terms on the right hand side of Eq. (2) need be considered. If the recoil electron has zero velocity, we have a special case in the predictions of the theory. The equation for this case is.

$$h\nu = h\nu' + h\nu_s. \tag{3}$$

[1] A. H. Compton, X-rays and Electrons, p. 260.
[2] A. H. Compton, X-Rays and Electrons, p. 270.
[3] A. H. Compton, X-Rays and Electrons, p. 285.

When converted into wave-lengths, the equation becomes,

$$\delta\lambda = \frac{\lambda^2}{\lambda_s - \lambda} \tag{4}$$

where $\delta\lambda$ is the change in wave-length of the incident radiation, λ_s the characteristic wave-length of the s^{th} level, and λ the wave-length of the incident radiation. This is the x-ray analogue to the Raman effect with light.

Davis and Mitchell,[4] Mitchell,[5] and Davis and Purks[6] have reported a fine structure, predicted by this special case of scattering by bound electrons, with various materials used for scattering. They have also reported the existence of spectral lines whose wave-lengths are given by the equation

$$\delta\lambda = \frac{h}{mc}(1 - \cos\phi) + \frac{\lambda^2}{\lambda_s - \lambda} \tag{5}$$

except that the constant h/mc should be about 9 percent less than the theoretical value 0.0243A. DuMond[7] has observed small humps on the modified line scattered from Be, but was unable to interpret them in the above fashion. Coster,[8] Ehrenberg,[9] and Kast[10] were unable to detect any fine structure with scatterers of graphite and aluminum.

All the investigators who observed the fine structure lines used the double crystal spectrometer, while those who did not observe them, used a single crystal spectrograph. With this in mind, the writer has reexamined the spectrum of scattered x-rays using a double crystal spectrometer. Two separate experiments have been performed.

Method I

X-rays were scattered from a block of graphite in air at about 109° with a divergence of angle of $\pm 9°$. The scattered radiation was limited by two lead slits before striking the first crystal of a double crystal spectrometer. The radiation reflected from the first crystal according to Bragg's law, was again reflected by the second crystal. The reflection from the second crystal entered an ionization chamber after passing through three lead slits. The ionization produced in the methyl bromide in the chamber was measured by a Compton electrometer. A diagram of the apparatus is shown in Fig. 1.

Apparatus I

An oil immersed, full wave rectifier unit supplied voltages up to 60 peak kv and currents up to 110 ma. The unit was housed in a tank $14'' \times 25'' \times 34''$, and all parts at high voltage were immersed in oil except the insulated lead to the x-ray tubes.

[4] D. P. Mitchell, Phys. Rev. **33,** 871 (1929).
[5] B. Davis and D. P. Mitchell, Phys. Rev. **32,** 331 (1928).
[6] B. Davis and H. Purks, Phys. Rev. **34,** 1 (1929).
[7] J. W. M. DuMond, Phys. Rev. **33,** 643 (1929).
[8] Coster, Nature **123,** 642 (1929).
[9] Ehrenberg, Zeits. f. Physik. **53,** 234 (1929).
[10] Kast, Zeits. f. Physik **58,** 519 (1929).

Two metal x-ray tubes of small diameter were used. The distance from the center of the targets to the windows was 7/8 inch, and the aluminum windows were usually as thick as 0.05 mm. The size of the focal spots was adjusted by means of movable focal cups and in this experiment was the same as the size of the Mo buttons on the targets. Though the use of such large focal spots increased the divergence of the angle of scattering to some extent, it increased the possible input of the tube greatly. These tubes were connected in parallel, and a current of 50 ma was carried by each one. The potential usually used was 45 peak kv.

The double crystal spectrometer used was one made by the Société Genevoise. The first crystal table was graduated in one minute intervals, and its position could be estimated to a quarter of a minute. The second crystal table and ionization chamber circle were graduated in minutes, but by means of ocular micrometers, their positions could be read to one second of arc.

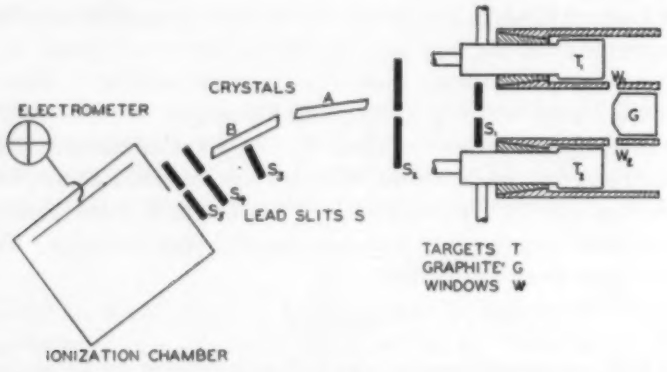

Fig. 1.

Crystals of calcite with their cleavage surfaces polished were used to reflect the x-rays. With the notation adopted by Allison and Williams,[11] the half width W at half maximum obtained with these crystals in the $(1,-1)$ position, was ten seconds of arc. With the crystals in the (1, 1) position, the value of W for Mo $K\alpha_1$ was 20 seconds. Though this resolution is not as good as that obtained by those[12] who have used cleavage faces of calcite, it is sufficient for the purposes of these experiments.

The ionization chamber was of brass, 10 cm long, and was filled with methyl bromide. There was a short lead to a Compton electrometer, which was equipped with a needle only 6 mm long. The capacity of the system was thus very small.

Method of Measurement I

(*a*) *The measurement of* $\delta\lambda$. The spectrometer was lined up by using direct radiation. There was sufficient intensity to observe the Mo$K\alpha_1$ and $K\alpha_2$ lines reflected from the second crystal, with a strip of fluorescent screen when

[11] S. K. Allison and J. H. Williams, Phys. Rev. **35**, 149 (1930).
[12] B. Davis and H. Purks, Phys. Rev. **34**, 181 (1929).

the room was partly darkened. Scattered rays were then sent through the same slit system, and the readings of the ionization current were taken as the second crystal was turned through intervals of 7.5 seconds of arc. A plate of Mo was occasionally used in place of the graphite as a check on the alignment of the system. The angular distance between the undisplaced α_1 line and any other line was measured from the plot of intensity vs. crystal angle. The value of $\delta\lambda$ was then calculated from the equation for the dispersion of the double crystal spectrometer,

$$\frac{\delta\theta_B}{\delta\lambda} = \frac{n_A}{2D\cos\theta_A} + \frac{n_B}{2D\cos\theta_B} \tag{6}$$

where the subscript A refers to the first crystal, the subscript B refers to the second crystal, and D is the grating space of calcite.

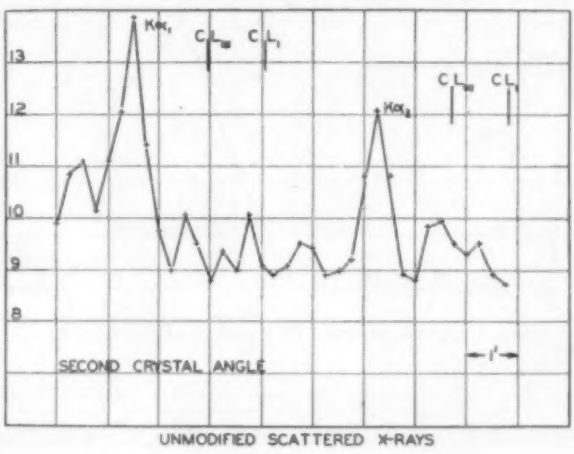

Fig. 2.

(*b*) *The measurement of* ϕ. In this experiment the measurement of the effective angle of scattering ϕ was not done with great care. However, it is sufficiently accurate to show a qualitative agreement between Compton's theory and this experiment. The extreme values of ϕ were got by geometrical considerations of the target-window-slit system, and the value of ϕ given is the arithmetic mean of the two extremes.

Result I

The results of this experiment are shown graphically in Figs. 2 and 3. Fig. 2 shows the undisplaced $K\alpha_1$ and $K\alpha_2$ lines as obtained from x-rays scattered at 109°. They appeared consistently at the same position, whether scattered radiation from graphite or fluorescent radiation from Mo was used. The space between these lines shows fluctuations, but no fluctuation greater than the experimental error encountered in working with as feeble radiation as was used here.

Fig. 3 shows the graph of Fig. 2 plotted on a smaller scale together with a continuation of the spectrum out as far as the modified line.

Readings were taken at smaller intervals than shown, but, since they agreed substantially with those plotted, are not included in the graph. Fig. 2 is the average of six typical curves, and the part of Fig. 3 not shown in Fig. 2 is the average of five curves.

Discussion and Conclusion I

The fine structure lines from a carbon scattering block, as reported by Davis and his collaborators, were found at the positions indicated by the lines CL_{III} and CL_{I} in Fig. 2. It will be seen that the present experiments give no indication of lines in these positions.

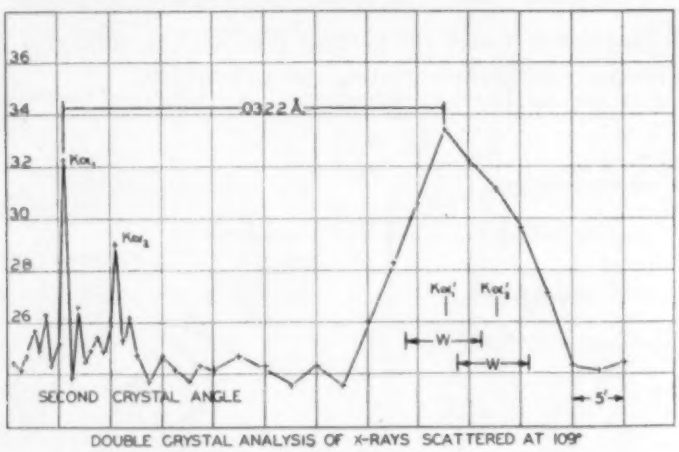

Fig. 3

Carrelli[13] has made a calculation to learn upon what factors the intensity of these fine structure lines depends. If the photon incident upon the atom lifts a K electron to a $1s$ level, the intensity I of the shifted line should be proportional to the following expression:

$$I \sim Z^{-3} \frac{\left[1+\frac{E_e}{E_u}\right]^4}{\left[1+\frac{E_e}{4E_u}\right]^4}.$$

If the incident photon lifts a K electron to the $2p$ level, the intensity I of the shifted line should then be proportional to:

$$I \sim Z^{-5} \frac{E_e}{E_u} \frac{\left[1+\frac{E_e}{4E_u}\right]^4}{\left[1+\frac{4E_e}{E_u}\right]^6}.$$

[13] A. Carrelli, Zeits. f. Physik **61**, 632 (1930).

Somewhat similar expressions are given for the case of an L electron being lifted to a $1s$ or a $2p$ level. These latter two expressions show that the intensity of a line caused by the removal of an L electron, is less than that for the removal of a K electron. In order to obtain greater intensity of the lines, the following three conditions must be fulfilled:

(a) Use substances presenting semi-optical lines. (b) Use substances of low atomic number. (c) Use exciting wave-lengths, directions of observation, and substances for which the ratio E_e/E_u is very high. Here E_e is the kinetic energy of the electron emitted for the Compton effect in one particular direction, and E_u is the energy of the level from which the electron is lifted. These are fulfilled reasonably well in this experiment, so that nearly the optimum intensity could be expected.

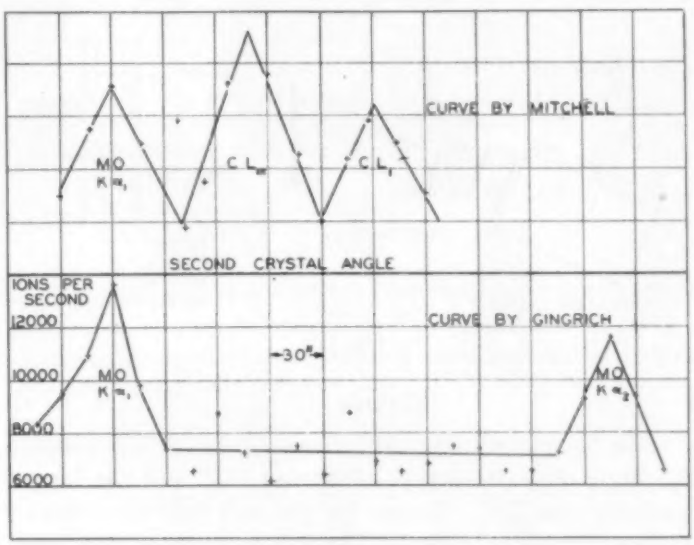

Fig. 4.

In Fig. 4 is reproduced a curve published by Mitchell[4] reporting fine structure lines in x-rays scattered from carbon. It will be noted that the modified lines are of the same order of intensity as the unmodified lines. This is true also for the curves published by Davis and Mitchell[5] and Davis and Purks.[6] Fig. 3, on the other hand, shows no indication of fine structure lines between Mo$K\alpha_1$ and $K\alpha_2$ of greater intensity than 15 or 20 percent of the undisplaced α_1 line. The fluctuations between the bases of α_1 and α_2 could hardly be interpreted as fine structure lines since they do not have the width characteristic of a true line resolved by the spectrometer. The separate spectra taken had larger fluctuations than the average of all six spectra, but no consistently high readings were obtained at points between the α_1 and α_2 lines. Since the ionization produced by one alpha-particle during the time of taking an observation is comparable with the ionization measured, it is evident that the chance fluctuations observed could easily be produced by a slight radioactivity of the chamber.

Bearden[14] reported the completion of a similar experiment, shortly after these results were obtained. His conclusions are essentially the same as the writer's,[15] except that in his experiment, the intensity of the fine structure lines could be no more than 10 percent of the undisplaced α_1 line. Bearden used a scattering block inside the tube, and since a slight deposit of the target metal on the scattering block would produce relatively strong fluorescent rays, his method has been criticized by those who report evidence of fine structure. However, Bearden's chemical analysis of the scattering block may invalidate this criticism. This objection does not hold in the present experiment.

From this experiment, the conclusion is drawn that no fine structure of intensity greater than 15 or 20 per cent of the unmodified radiation is present in radiation scattered at 109° by graphite.

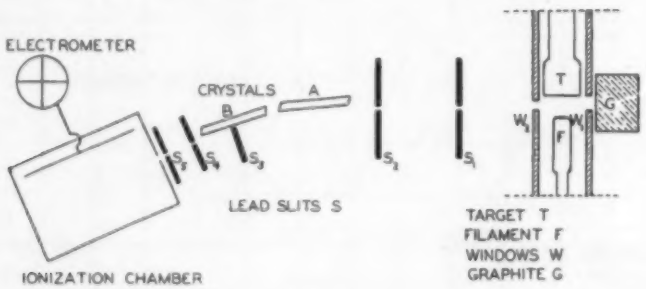

Fig. 5.

Method II

X-rays were scattered at 161° from a block of graphite in air. The smallest angle of scattering possible was 153° and the largest angle of scattering possible was 175°. Except for the fact that the x-rays were scattered at a different angle, the method in this experiment was essentially the same as that in the first experiment. A diagram of the apparatus is shown in Fig. 5.

Apparatus II

The same source of high voltage was used in this experiment as was described under Apparatus I.

One metal x-ray tube of small diameter was used. The distance from the center of the target to the windows was 7/8 inch. This tube had two windows instead of one as in the first apparatus. The second window was diametrically opposite the first window. The size of the focal spot was adjusted with a movable focal cup. With a voltage of 50 peak kv across the tube, a current of 100 ma. was used through the tube. Occasionally only 60 ma. were used.

The same double crystal spectrometer, crystals, and detecting devices were used as are described in Apparatus I.

[14] J. A. Bearden, Phys. Rev. **35**, 1427 (1930).
[15] N. S. Gingrich, Phys. Rev. **35**, 1444 (1930).

METHOD OF MEASUREMENT II

Measurement of ϕ. In order to measure accurately the effective angle of scattering, the following procedure was followed. Pinhole pictures of the focal spot were taken, and the variation of intensity of the x-rays from various

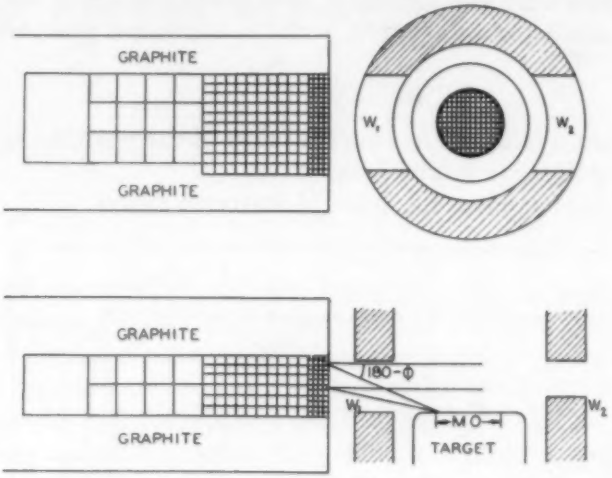

Fig. 6.

portions of the target was measured. The Mo target was then marked off with millimeter squares, as indicated in Fig. 6, and a weighting factor was associated with each square in accordance with the relative intensity of x-

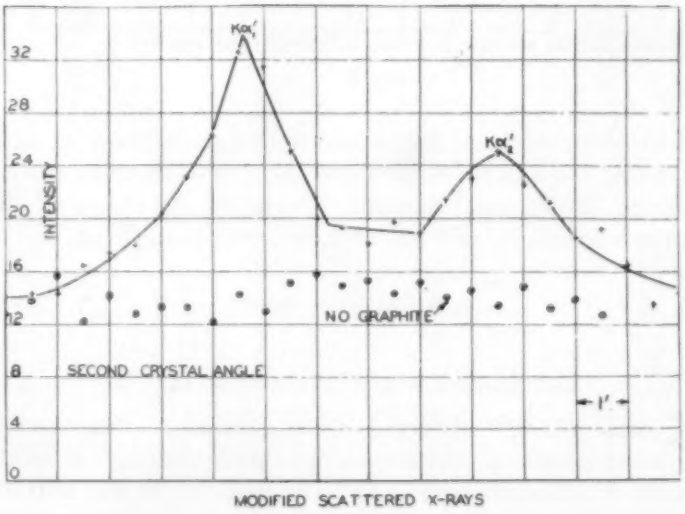

Fig. 7.

rays from this square. The scattering block was then divided into small segments of volume as shown.

The angle of scattering caused by the x-rays from each element of target area to each element of scattering volume was calculated geometrically. The

cosine of each angle thus obtained was multiplied by the number representing the relative intensity of the x-ray from the area used, was multiplied by the relative volume of the element of scatterer considered, and then by a factor correcting for the absorption of the x-rays in the graphite. These values of the weighted cosines were then averaged. The grand average of the weighted cosines as thus calculated was 0.9479, with an estimated probable error of ± 0.003.

Results II

Fig. 7 shows the average of five curves taken of the modified beam. The α_1 and α_2 modified lines are definitely separated.

Fig. 8 shows the complete spectrum of scattered x-rays.

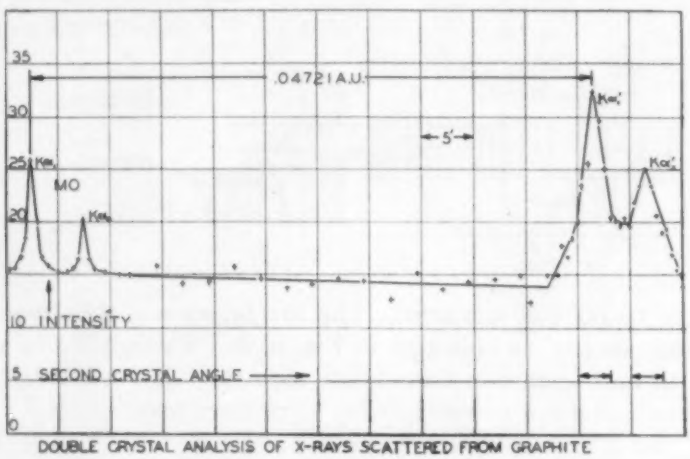

Fig. 8.

The value of $\delta\lambda$ obtained from five separate determinations, as calculated from Eq. (6), using $D = 3.02904$A, was $0.04721 \pm .00003$A when the probable error is calculated in the usual manner. Using for the cosine of the angle of scattering the average value 0.9479 ± 0.003, we obtain from Eq. (1),

$$\frac{h}{mc} = 0.02424 \pm .00004.$$

Discussion and Conclusion II

Kallmann and Mark[16] obtained fairly accurate measurements of the change in wave-length of scattered x-rays with the single crystal photographic method. From scattering at 72°, the value of $\delta\lambda$ was 0.0170A, and by substitution in equation (1), one finds that $h/mc = 0.0246$A. From scattering at 90°, the value of $\delta\lambda$ was 0.0241A and that of h/mc was 0.0241A.

H. M. Sharp[17] has measured $\delta\lambda$ using the single crystal, and, combining this value with his value of (1-cos ϕ), obtains the experimental value

[16] H. Kallman and H. Mark, Naturwiss. **13**, 297 (1925).
[17] H. M. Sharp, Phys. Rev. **26**, 691 (1925).

$$\frac{h}{mc} = 0.02432 \pm .00009A.$$

The value of the ratio h/mc as calculated from the accepted values of the constants differs according as the deflection or the spectroscopic value of e/m is used. In the former case, Birge[18] finds

$$\frac{h}{mc} = 0.02428A$$

and in the latter case

$$\frac{h}{mc} = 0.02417A.$$

The value found from the present experiment lies between these extremes. There is thus no indication of a departure of the experiments from the predictions of Compton's theory of scattering.

These experiments were carried out under the supervision of Professor A. H. Compton and the writer is indebted to him for his encouragement and helpful suggestions. The writer also wishes to express his appreciation of the many very helpful practical suggestions given by Dr. R. D. Bennett.

[18] R. T. Birge, Phys. Rev. Supplement 1, 1 (1929).

THE SCATTERING OF FAST ELECTRONS BY METALS. II. POLARIZATION BY DOUBLE SCATTERING AT RIGHT ANGLES

By Carl T. Chase
New York University, University Heights, N. Y.

(Received July 28, 1930)

Abstract

The first paper of this series discussed methods of counting fast electrons, a consideration of which has shown the need for further experiments looking for polarization of fast electrons. The present paper concerns a search for polarization by double scattering at right angles, using radium E as a source, and a sensitive gold leaf electroscope to detect the arrival of the scattered electrons, the slower electrons being eliminated from the experiment. A peculiar type of polarization appears, which can be described as follows, using the notation of previous papers. At moderate electron speeds the number counted in the configuration called 0° is greater than the number counted at 180°. This effect does not appear for very slow electrons. As the speed of the electrons approaches that of light, the above type of polarization persists, and another type appears, superposed upon the first; the number counted at 270° becomes greater than the number counted at 90°. Previous experiments of a similar nature, in which one or the other of the above effects appears, are discussed.

THE reasons for performing this work are inherent in the results, and will accordingly not be discussed at this point. We proceed immediately to a description of the experiment, which will be followed by a comparison with other similar experiments.

A sectional diagram of the apparatus used is shown. In this diagram, lead shielding is depicted by double cross-hatching, the brass apparatus itself being shown in section by single cross-hatching. The two lead targets, as well as the radium source, are completely inked in. The sketch is drawn to scale. The radium source consists of a number of old radium emanation tubes containing radium D, E, etc., cut in half and bound in a bundle, open ends toward the upper target. The source is firmly attached to the shaft carrying the upper target, which can be rotated by the handle shown at the top, the shaft passing through the cover in a ground joint. By this means the configuration of the electron path is altered. The apparatus is kept evacuated by means of the tube shown at the right. The window at the immediate left of the lower target is of aluminum, 0.03 mm thick, while the window in the wall of the electroscope is of aluminum, 0.04 mm thick.

The case of the electroscope is made of lead, as shown, the only openings being two circular windows for observing and illumination, covered with glass; the window covered with aluminum for the entrance of the electrons; and the small opening at the left through which a glass tube projects. A wire through this glass tube serves to charge the leaf system. The case contains a drying agent. This type of electroscope has proved most satisfactory.

The lead case protects the leaf to a large extent from the soft radiations always present, from the laboratory walls, air, etc. By having the leaf system completely enclosed in the case, any ionization present in the air from whatever cause is not able to affect the rate of fall of the leaf, this making for consistent operation at all times. A further benefit is that the sulphur plug, on which the leaf system is mounted, does not become contaminated, as would be the case if it projected into the air of the room. The electroscope is sensitive to vibration, and its rate of fall for a given amount of entering radiation changes to some extent with the temperature of the room in which it is used, but with ordinary laboratory precautions it has proved to be the most sensitive and reliable instrument for detecting small amounts of ionizing radiation which the writer has ever used. The rate of fall of the leaf is observed by means of a microscope with a magnifying power of about twenty-five dia-

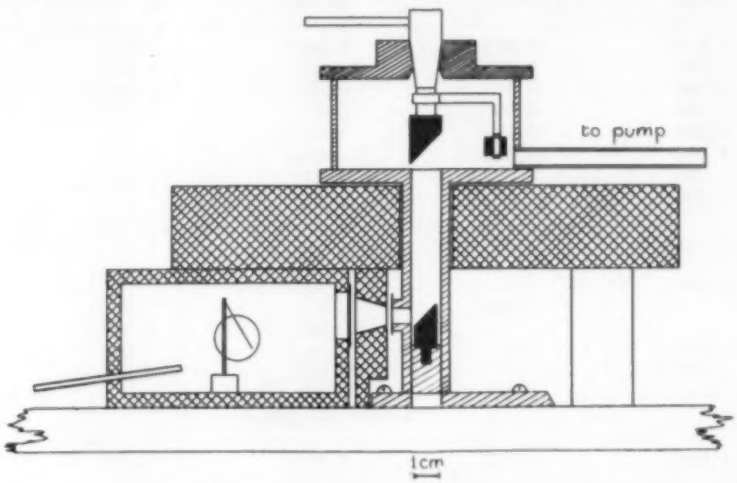

Fig. 1. Diagram of apparatus.

meters, provided with a scale in the eyepiece. This electroscope is far more sensitive than the point-discharge counters which we have used, to say nothing of its infinitely greater reliability and ease of use. The one disadvantage, that it is very sensitive to gamma-rays, can be eliminated by proper shielding. We may mention here that readings should not be taken immediately after charging the leaf, for if any spark passes in the charging process, ions are formed which are a few moments in disappearing.

If very fast electrons are desired, one thinks immediately of using radium C as a source. Radium E emits very fast electrons, but the peak of intensity in the velocity spectrum of radium C occurs in a region of higher velocity than is the case for radium E. By using plenty of radium E, however, and screening out the slower rays, it is possible to obtain a sufficient number of electrons with high enough speeds. Radium C emits powerful gamma-rays, while radium E emits gamma-rays of very feeble intensity and penetrating power. We have accordingly decided to continue to use radium E as a source, cutting out the slower electrons by means of absorbing screens

placed in front of the electroscope. We are concerned here with electrons having speeds from about 0.7 to 0.95 of the velocity of light.

The configuration shown in the diagram is called 0°. The configurations 90°, 180°, and 270° are obtained by rotating the plug, upper target, etc., clockwise as seen from above.

Counts are taken in several ways. First, counts are taken continuously around the circle, taking the time required for the leaf to drift over a given part of its scale at the settings 0°, 90°, etc., continuing round and round as long as possible. Then counts are taken alternately at two of the positions,

TABLE I. *Numbers refer to relative counts, and are not corrected for the "zero rate of fall" of the electroscope. This is done on the curve. The experimental error is one percent, obtained from the accuracy obtainable in taking individual readings, and from a consideration of the final data.*

At 0°	At 90°	At 180°	At 270°	Weight
1.000	0.972	1.009	1.024	1
1.000	0.975	1.075	1.075	1
1.000	0.997	0.986	1.005	1
1.000	0.990	0.986	1.015	1
1.000	0.988	1.000	1.008	1
1.000	0.994	0.976	1.010	1
1.000	1.034	1.041	1.044	1
1.000	—	0.950	—	4
—	1.000	—	1.030	3
—	1.000	—	1.040	3
—	—	1.000	1.020	2
1.000	—	0.933	—	1
—	1.000	—	1.030	2
—	—	1.000	0.969	2
1.000	—	—	1.003	1
1.000	—	1.037	—	2
—	1.000	0.933	—	2
		Means (Weighted)		
1.000	0.993	0.985	1.021	

counting repeatedly at first one, then the other of the two, to get a determination of the ratio of the numbers of electrons counted in these two configurations. The process is then repeated for another pair, etc. The results are shown in tabular form. The weight attributed to each run is determined by the relative number of counts made in each position. The weighted average of all the runs is plotted.

We discuss first the asymmetry as between the configurations 90° and 270°. This asymmetry has not been predicted in any theory. It has been observed first by Cox, McIlwraith, and Kurrelmeyer,[1] in experiments using point-discharge counters, being observed in two separate pieces of apparatus of different size. It also appeared in a third apparatus of the same nature made by the writer,[2] but not in later experiments[2] which seemed at the time to be the most consistent and conclusive of the entire series; these experiments have been rediscussed in a previous paper[3] to which the reader is re-

[1] Cox, McIlwraith, and Kurrelmeyer, Proc. Nat. Acad. Sci. **14**, 544 (1928).
[2] Chase, Phys. Rev. **34**, 1069 (1929).
[3] Chase, Phys. Rev. **36**, 984 (1930).

ferred. The argument was that the point-discharge counters have been found by experiments with a magnetic beta-ray spectrograph to register only the slower electrons unless the potential applied to the counter is raised to such a high value as to render the life of the point, the time during which it gives reliable results, very short. In the three cases mentioned above in which this effect appeared, the apparatus was so constructed that the electrons had to pass through about 0.2 mm of mica and aluminum, which cut out the slower rays. The small number of electrons left forced the use of high voltages on the counters, in order to obtain any electron counts at all. These high voltages in turn made the counters more unreliable than ever, but also made them sensitive to the very fast electrons. Gamma-ray counts were predominant in the total count, but in the positions 90° and 270° should have been of equal intensity.

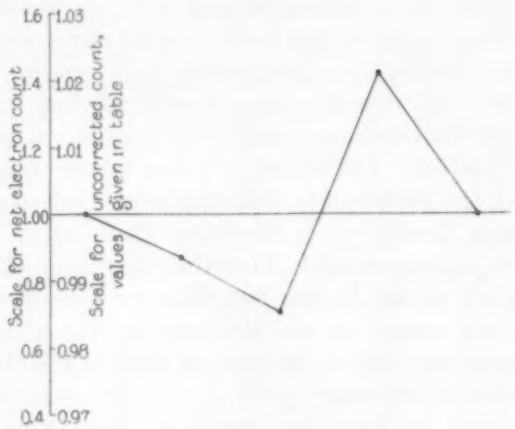

Fig. 2.

The experiment of Chase which gave a negative result eliminated the gamma-ray counts, and by decreasing the window thickness to 0.04 mm increased the number of electrons which arrived at the counter, these added electrons being the slower ones which had previously been excluded. With more electrons to count, the counters could be operated at lower voltages, sufficiently low for the points to give consistent results for a whole day. We have shown[3] that these consistent results did not include the faster electrons, and any polarization effect is predicted for fast electrons. At the time the consistency of the results were convincing, and it was thought that electrons having speeds of say 0.5 of the velocity of light were to be considered as fast. We now see that for the purpose of discussing the effect with which we are concerned, these speeds are to be regarded as slow, and speeds of at least 0.7 of the velocity of light are necessary.

The following can be said of the present experiments; the asymmetry between the counts at 90° and 270° is always observed, which was in no sense true before. Not only every single run, but even all the readings in every run, with few exceptions, show the effect. As an interesting sort of check, the apparatus which had previously given a negative result[2] was set

up again; with counters used as they had been before, at lower voltages, the results were negative as before, but with high voltages on the counter, high enough to ruin the point within an hour or two, the effect was very likely to appear. Making no changes except in the voltage on the counter, the effect could be accentuated or suppressed.

It will also be noted that in the average more electrons are counted at 0° than at 180°, though this effect is not so consistently observed as that between the other two positions. The position of the point at 180° on the curve must therefore be regarded as the least reliable of the set.

Mott has predicted[4] on the basis of the Dirac electron theory that this experiment should show a polarization effect in that an asymmetry should be observable between the two positions 0° and 180°. This effect is supposed to be more definite for fast electrons and heavy scattering materials. He predicts equal counts for the positions 90° and 270°. A previous experiment of the writer[2] showed an effect of this nature, more electrons being counted in the 0° position than in the opposite position by 4 percent. Nothing was claimed for this result, because the targets were so close together that it seemed plausible that the electrons would find it easier to get through the apparatus in the 0° position. The targets are now farther apart, since fewer electrons per second are permissible with the increased sensitivity of the electroscope, and beam divergence is much less than before. The previous objection is, therefore, no longer valid. That the effect is not due to the penetration of gamma-rays is shown by the fact that the presence or absence of the lead shield between apparatus and electroscope had little if any effect. A piece of paper held in the path of the rays, in front of the electroscope, cut down this asymmetry to a very small figure.

A similar experiment has been performed by Rupp,[5] but slower electrons from a filament were used, and instead of scattering the electrons at right angles, the rays were reflected at grazing incidence. He observes an asymmetry of 12 percent with more electrons counted at 0° than at 180°, for filament electrons accelerated through 80 kilovolts. The asymmetry is less for 40 kilovolt electrons, and disappears for 10 kilovolt electrons. The above applies to gold targets; he does not observe the effect for slow electrons with gold targets, nor for fast electrons with beryllium targets. Neither does he observe the asymmetry between 90° and 270°, which is in accordance with our contention concerning the electron speeds necessary to observe this effect.

It has not been shown that Mott's prediction applies directly to reflection at grazing incidence. Further, one might say that electrons would find a freer path through Rupp's apparatus in the 0° position, especially the fast ones. His results, however, appear to be beyond argument of this sort, since his effect is not observed for light targets, all else remaining the same.

We may say in general that there are several unsatisfactory things about this experiment. For instance, electrons hitting the lead targets produce

[4] Mott, Roy. Soc. Proc. **A124,** 425 (1929).
[5] Rupp, Zeits. f. Physik **61,** 158 (1930).

secondary gamma-radiation, that from the lower target being able to affect the electroscope. Also, secondary gamma-radiation from the upper target may eject electrons from the lower target which will be counted. Besides, we do not know how the electrons which are finally counted are related to those originally falling on the upper target. They may be the same ones, either with the original velocity, or, which is more probably the case in view of experiments with absorbing screens of paper before the electroscope, with diminished velocities. Lead screens cannot be used to test this point, since electrons produce secondary gamma-rays when they fall on lead. For this reason we used paper screens. The counted electrons may also be secondary, tertiary, etc. electrons produced by the primaries. These points will have to be tested in auxiliary experiments.

The next paper will deal with scattering at right angles, but the electrons will be those which have been scattered by transmission through thin foils, in contrast to the present case in which diffusely reflected electrons were used. We shall return later to the present experiment using reflected electrons, in order to get a more exact measurement of the effect. It seems better to postpone this until we have found in how many ways the effect can be obtained.

AN EXPERIMENTAL DETERMINATION OF THE CHANGE IN TEMPERATURE ACCOMPANYING CHANGE IN MAGNETIZATION OF IRON[1]

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(Received July 21, 1930)

Abstract

Apparatus.—An apparatus is described which permits the measurement of the change in temperature of a ferromagnetic material consequent upon a change in its magnetization. The test specimen, of peculiar form and construction, is placed in a specially designed calorimeter. Around this is wound a solenoid which furnished the magnetizing field. Changes in temperature are measured by means of 102 thermocouples connected in series to a sensitive galvanometer. Methods are described for minimizing thermal and thermoelectric disturbances. The sensitivity of the system is such that a temperature change of 2.26×10^{-6} °C can be detected. This corresponds to a thermal energy change of 87 ergs per cm³ for steel.

Results.—Results are reported on for two specimens of carbon steel containing 1.08 percent and 1.35 percent carbon respectively. Detailed data are presented showing the relationship between temperature change and magnetizing field as the material is carried through various symmetric and asymmetric cycles of magnetization.

The following is typical of a symmetric cycle which starts with the steel in a saturated condition. As the magnetizing field is diminished from +290 to +20 gauss the temperature of the steel rises gradually; this is followed by a very marked cooling between +20 and −8 gauss; if the magnetizing field is further diminished from −8 gauss through the coercive force (−9.6 gauss) to −90 gauss a sudden rise in temperature indicates the release in this region of the major portion of the hysteretic energy; between −90 and −290 gauss the steel cools gradually.

Temperature changes for smaller cycles of magnetization are qualitatively the same as for the large cycle, except that the second cooling may be absent. Similar sharply defined regions of heating and cooling are characteristic of the different asymmetric cycles investigated.

It appears that the total amount of hysteretic heat developed depends upon the rate of performance of the cycle, at least for those cycles which nearly saturate the steel. A rapid traversal yields a greater total heat than a slow traversal.

A—Object

THE object of this research is to measure the spontaneous change in temperature of a specimen of iron which occurs when the magnetic state of the iron is altered in any way. As was pointed out by Larmor,[2] calorimetric data of this sort are essential to the formulation of a theory of the energy in a magnetized medium. The experimental results here reported are intended as a contribution to such a theory.

What follows will be better understood if it is stated at once that the experiment here contemplated necessitates the measurement of a change in

[1] The author's preliminary report of this work appeared in Nature **123**, 797 (1929).
[2] Larmor, Proc. Roy. Soc. **71**, 239 (1903).

temperature of the order of one hundred thousandth of a degree Centigrade in a space surrounded by a magnetizing current dissipating as much as four kilowatts of power.

B—Apparatus

(a) **Material.** The magnetic material used in this research is a carbon steel commercially known as "drill rod."

The sample of drill rod which yielded the observations reported in *Nature*[1] contained 1.35% carbon. Fig. 1 is a microphotograph of this material; it shows tiny globules of cementite (Fe_3C) in a matrix of *almost* divorced pearlite.[3]

The material used in the present series of experiments contains 1.08% carbon. A microphotograph of a sample of this steel (Fig. 2) shows it to be an annealed mechanical mixture of cementite in a ferrite matrix. The coarse globules of cementite are characteristic of *completely* divorced pearlite.

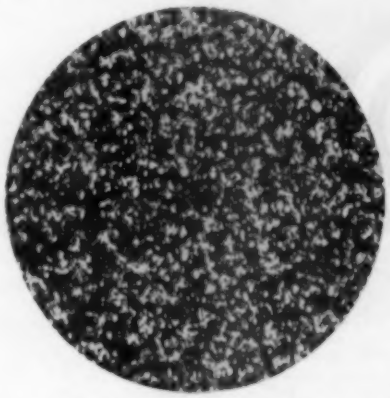


Fig. 1. Microphotograph of 1.35% carbon steel (500x).

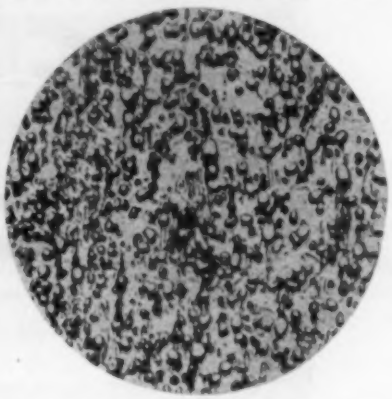


Fig. 2. Microphotograph of 1.08% carbon steel (500x).

(b) **The test specimen.** The test specimen consists of 104 bars of the 1.08% carbon steel 1 mm in diameter (drill rod size #57), selected for magnetic uniformity. These bars are mounted on the surfaces of seven concentric coaxial cylinders, the lengths of the bars in the several cylinders being so adjusted as to give the aggregate the form of an ellpsoid of revolution of major axis 60 cm and minor axis 3.4 cm. The frame for holding the bars consists of six hard rubber disks held together with brass rods.

Between the iron bars are mounted an equal number of copper bars of the same diameter and length. The function of these copper bars is described below.

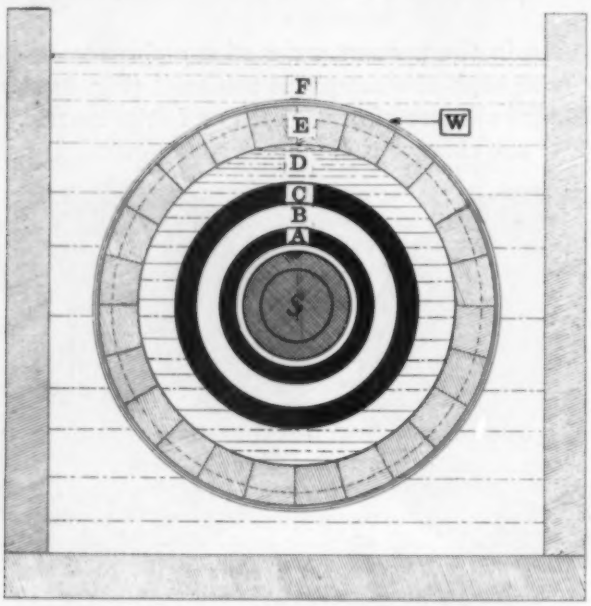
(c) **The calorimeter.** Fig. 3 shows a cross-section of the calorimeter in which the experiment was performed. The specimen *S* is imbedded in rice flour,[4] and placed in an evacuated glass tube 5 cm in diameter about 1

[3] Pearlite is a mechanical mixture of iron and iron carbide containing about 0.9% carbon.

[4] International Critical Tables—Thermal Conductivities of Powders. Vol. II, p. 315. (The thermal insulation of rice flour plus a vacuum is here shown to be superior to the thermal insulation of a vacuum alone).

meter long, the inner surface of which is silvered and electrically grounded. The glass tube is surrounded by a hard rubber tube, *A*, an air space, *B*, and a second hard rubber tube, *C*. The wall thickness of the hard rubber tubes is approximately 1 cm. *E*, is a redwood cylinder, 1.8 cm thick, upon which the magnetizing solenoid, *W* is wound.

A centrifugal pump, delivering 1.5 liters per second, maintains a continuous circulation of water through the space *D* and an auxiliary tank not shown in the figure. The temperature of this water is controlled by means of a mercury-in-glass thermostat[5] operating a 1000 watt incandescent light



SECTION OF CALORIMETER-SOLENOID.

Fig. 3.

bulb, both located in the tank. Water from the city mains at a temperature below 15°C is added continuously to the circulating water to compensate for evaporation and leakage, and for the heat from all other sources except the lamp. The fluctuations in temperature of the water in the space *D* under operating conditions have a maximum amplitude of 0.01°C with a period of 5 seconds.

A continuous flow of water, *F*, from the city mains surrounds the solenoid. This flow effectively removes most of the power dissipated in the coil, which may be as much as 4 kilowatts.

The calorimeter just described entirely eliminates thermal disturbances as a source of error in the measurements.

(d) **The solenoid.** The solenoid consists of two layers of #16 B and S gauge enamelled, double cotton covered copper wire. The insulation was

[5] Eight-inch metastatic thermoregulator made by the American Instrument Company.

saturated with asphaltum paint as the coil was wound. The winding is 114 cm long and 19 cm in diameter. It is tapered at an angle of 1° 16′ for a distance of 27 cm at each end in order to secure greater uniformity of field.[6] The magnetic field does not vary more than 1% over the space occupied by the specimen.

(e). **The thermocouple system.** Temperature changes of the 104 iron bars constituting the test specimen are measured by means of 102 thermo-

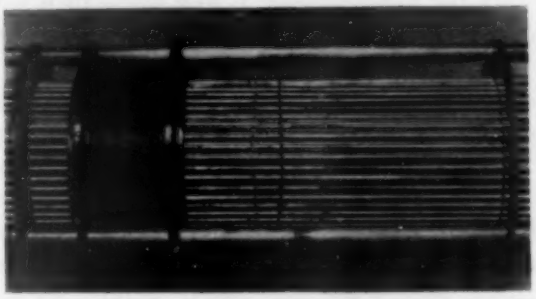


Fig. 4. Photograph of the assembly of rods and thermocouples.

couples in series. These thermocouples are constructed by connecting adjacent iron and copper bars alternately with short lengths of #40 copper and #34 constantan wire. These bits of wire are soldered to the bars with ordinary soft solder. The temperature of the copper bars, being comparatively unaffected by the magnetic field, thus affords a reference point from which to measure a change in temperature of the iron bars.

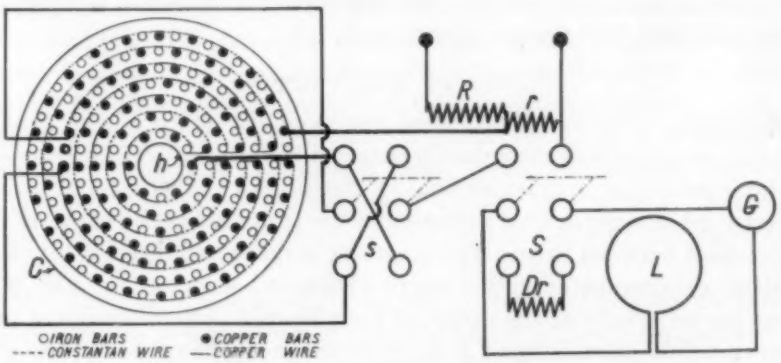


Fig. 5. Thermocouple circuits.

Fig. 4 shows the assembly of copper and iron rods in which the thermocouples may be seen to the right of the coil. This coil, which is displaced to the left in the photograph, is used in the magnetic measurements to be described later.

Fig. 5 is a diagram of the thermocouple and galvanometer circuits. The thermocouples are connected in series so as to form two groups of 51 couples

[6] L. Houllevigue, J. de Phys. [3] **7**, 466–468 (1898).

each, which groups may, in turn, be connected either in series aiding or in opposition by means of switch *s*. Switch *S* connects the galvanometer to the thermocouples or to an equal non-inductive resistance *Dr* which serves as a dummy. Resistances *R* (400000 ohms) and *r* (0.400 ohms) constitute the calibrating potentiometer. The resistances *r*, *R*, *Dr*, and the switches *s* and *S*[7] are placed in a wooden box covered with heavy felt. The switches are operated at a distance by piano wires passing through holes in the sides of the box. In series with the galvanometer, *G*, is a single turn of wire, *L*, 10 cm in diameter, so placed as to compensate entirely the inductive effect of the lead wires.

The galvanometer is a Leeds and Northrup d'Arsonval type HS 2285x with a critical damping resistance of 12 ohms, a period of 10 seconds and a sensitivity of 103 mm per microvolt at a scale distance of 6 meters. It is mounted in a box filled with cotton batting on a specially constructed suspension which reduces the effects of vibration to a satisfactory minimum. The metal platform of the suspension is grounded.

Since thermal disturbances are completely eliminated as a source of error, the accuracy of the thermal measurements is limited solely by the magnitude of the variation of the parasitic electromotive forces in the galvanometer circuit. With the precautions mentioned above the maximum variation in the parasitic electromotive forces over a period of 3 hours is 0.1 microvolt. This appears in the form of a slow drift in the galvanometer zero, amounting in all to 10 mm under operating conditions. Since the time required to complete a single observation is not more than 5 minutes the error due to this source is negligible. Accordingly the accuracy of the method is equal to its sensitivity, and permits the detection of a change in temperature of the iron of 2.26×10^{-6} degrees Centigrade.

C—Method of Measurement

(a) **Magnetic.** The specification of the magnetic state of the iron involves the determinaton of the relation between the magnetic field intensity, *H*, and the intensity of magnetization, *J*. Because of the ellipsoidal form of the specimen the magnetic field intensity in the iron bars is the same as that in the interspace between them. This quantity is measured directly by means of a ballistic galvanometer and a small calibrated solenoid (*h*, Fig. 5) of 1041 turns placed axially at the center of the ellipsoid. The intensity of magnetization can then be calculated if the total magnetic flux through the ellipsoid is known. This quantity is likewise measured ballistically, with the aid of a 48 turn coil (*C*, Fig. 5) of known area wound around the ellipsoid at its center. The change in intensity of magnetization in the iron can now be obtained as follows:

Let

ΔH = change in the magnetic field intensity as measured above,
ΔF = change in the total flux through the coil *C*,

[7] Walter P. White, Journ. Amer. Chem. Soc. **33**, 1856 (1914), also Journ. Amer. Chem. Soc. **33**, 2296 (1914).

ΔB = change in the magnetic flux density *in* the iron,

A = total cross sectional area of coil C,

a = cross sectional area of the 104 iron bars.

$A' = A - a$

Then

$$\Delta F = \Delta B a + \Delta H A'$$
$$= \Delta(H + 4\pi J)a + \Delta H(A - a)$$
$$= \Delta H A + 4\pi a \Delta J;$$

Hence

$$\Delta J = (\Delta F - \Delta H A)/4\pi a$$

The independent variable in the magnetic measurements is actually the magnetizing current, I. A specially constructed rheostat permits the variation of this current in steps of any desired magnitude by opening or closing knife switches. The values of J and H corresponding to specified values of the magnetizing current are now determined as follows: (1) The iron is first placed in a suitable cyclic state by repeated reversals of the magnetizing current. (2) The subsequent magnetic state of the iron is then varied in steps in any desired manner. (3) Corresponding $J - H$ curves are constructed by summing the successive increments in these quantities, obtained in the manner described above.

All the magnetic paths whose thermal relations are here investigated start at some point on a hysteresis loop. It is, therefore, important to determine these loops as precisely as possible. Errors intrinsic to the step by step summation method can be detected by reducing the number of steps to one. This gives an overall check on the end points. The absolute values of J are calculated from its maximum value. The latter is assumed to be $\frac{1}{2}$ the observed change in J in passing in a single step from one tip of the hysteresis loop to the other. The absolute values of H are calculated from its value when $J = 0$, i.e. from the coercive force. When $J = 0$, H is simply the magnetic field intensity of the solenoid alone. The corresponding solenoid current is obtained graphically by plotting J against the current. The value of H when $J = 0$ is then calculated from the current and the constant of the solenoid.

(b) **Thermal**. As stated above, the object of this research is to measure the changes in temperature of the iron which accompany changes in H and J, produced and evaluated in the manner just described. It is assumed that this temperature change occurs simultaneously with the change in magnetization. Immediately thereafter the induced change in temperature decays logarithmically[8] due to radiation and to conduction through the rice flour and across the thermocouple wires. The experimental procedure for obtaining the initial value of this quantity is as follows:

1. The thermocouple galvanometer is switched from the dummy resistance to the thermocouples and the deflection noted. This deflection of

[8] The average thermal time constant is 32 seconds.

about 10 mm is due to the constant parasitic e.m.f.'s in the switches and the thermocouple leads. It is taken as the zero in reckoning subsequent deflections. The small value and the constancy of this quantity indicate establishment of thermal equilibrium in the calorimeter.

2. The galvanometer is switched back to the dummy resistance.

3. At time $t=0$ the desired change in magnetizing current is effected.

4. Immediately thereafter the galvanometer is switched from the dummy resistance to the thermocouples.

5. At $t=10$ seconds the galvanometer deflection is noted. It is again noted at $t=20$ seconds.

6. These galvanometer deflections are directly proportional to the corresponding thermal *emf*'s. (1 mm = 0.01 microvolt = 2.26×10^{-6}° C.) The *emf* corresponding to the temperature at time $t=0$ is obtained by extrapolation.

7. At the end of 5 minutes thermal equilibrium is reestablished and the operations 1 to 6 are repeated for a new change in magnetizing current. The magnetic path under investigation is thus traversed in successive steps of appropriate magnitude.

8. Curves showing the relation between temperature and magnetic field intensity for the complete magnetic process are constructed by summing the increments in temperature obtained in this manner. It is to be noted that a cooling of the iron is indicated by a galvanometer deflection in the opposite direction to that which indicates heating.

D. Experimental Results

(a). **Thermal relations.** The observed magneto-thermal relations are exhibited graphically in Figs. 6 to 12. As has been stated, the iron is placed in a cyclic state by a dozen reversals prior to each experiment, and is left in the condition of maximum magnetization for the cycle. In the figures the entire hysteresis loop of the cycle is shown by a curve in part solid and in part dotted. The solid curve shows the magnetic path actually traversed in the experiment. The direction of traversal is indicated by arrows and the starting point by a dot. The solid curve upon which the observations are plotted gives the relation between the total temperature change and the magnetic field intensity, as the path is traversed. This curve is constructed in the manner described in paragraph 8 of the preceding section. The temperature change indicated by an ordinate of this curve is the total change in temperature which would have resulted if no heat had been lost in the process of measurement. The temperature corresponding to the zero ordinate is 18° C and is the same for all curves.[9]

[9] The cooling observed at the upper end of the thermal curve of Fig. 6 was not revealed by the preliminary experiments reported in Nature, owing to outstanding parasitics and low sensitivity. Since these experiments were performed, the short period parasitics have been practically eliminated, and the galvanometer sensitivity has been doubled. A reexamination of this specimen, which contained 1.35% carbon, showed a cooling at the upper end of the thermal curve of approximately the same amount as that observed in the neighborhood of $H=0$, i.e., the curve is qualitatively the same as Fig. 6, the cooling effects being smaller.

Fig. 12 gives a plot of the data obtained for the so called "virgin curve" of magnetization. The iron was demagnetized by means of a 60 cycle alternating magnetic field of diminishing amplitude and also by the method of repeated reversals with identical results.

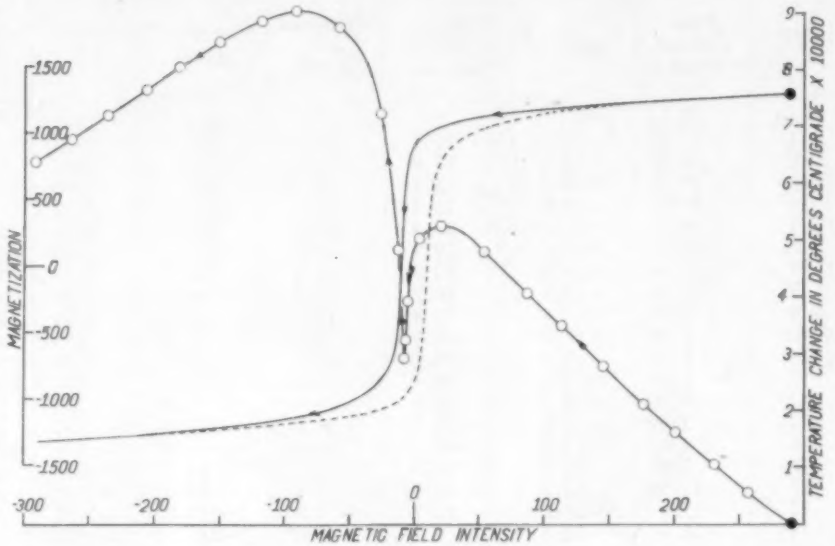


Fig. 6. The magneto-thermal relations associated with the largest hysteresis loop.

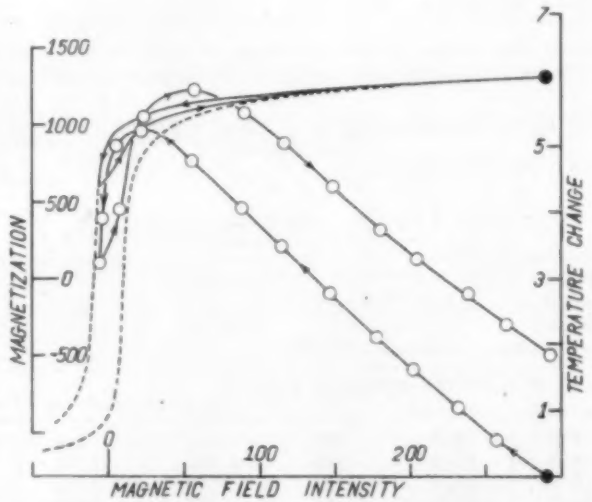


Fig. 7. The magneto-thermal relations associated with an asymmetric loop formed between $H = 290$ gauss, and zero impressed field.

Table I contains the experimental data for the curves of Fig. 6, and illustrates the way in which the curves are constructed. In this table the observed change in temperature is given in millimeters deflection of the

galvanometer. The calibration constant of the galvanometer thermocouple system is 2.26×10^{-6} degrees C per mm deflection.

TABLE I. *Data for curve of Figure 6.*

Step	Field Current (Amps.)	ΔH	ΔJ	Observed ΔT in mm	H gauss	J	Total Change Temp. (mm)
Start	35.1				284	1316	0.0
1	32.0	−27.3	− 14.1	19.5	257	1302	19.5
2	28.8	−26.3	− 15.0	21.3	231	1287	40.8
3	25.3	−29.8	− 18.1	24.2	201	1269	65.0
4	22.5	−23.9	− 16.3	21.3	177	1252	86.3
5	18.9	−31.1	− 23.4	28.8	146	1229	115.1
6	15.0	−32.3	− 29.1	30.5	114	1200	145.6
7	11.8	−26.4	− 19.3	24.5	87.7	1181	170.1
8	7.94	−33.3	− 46.8	31.0	54.4	1134	201.1
9	4.01	−32.8	− 79.4	19.3	21.6	1054	220.4
10	1.91	−17.0	−100.9	− 9.8	4.6	953	210.6
11	0.50	− 9.2	−206.0	−47.0	− 4.6	747	163.6
12	0.00	− 2.0	−150.4	−29.0	− 6.6	597	134.6
13	− 0.50	− 1.2	−234.0	−15.0	− 7.8	363	119.6
14	− 1.90	− 3.8	−790.0	82.5	− 11.6	− 427	202.1
15	− 4.01	−13.3	−406.0	103.3	− 24.9	− 833	305.4
16	− 7.97	−31.4	−216.7	65.5	− 56.3	−1050	370.9
17	−11.95	−33.3	− 88.0	11.8	− 89.6	−1138	382.7
18	−15.1	−26.6	− 42.7	− 7.5	−116.0	−1181	375.2
19	−18.9	−32.8	− 39.1	−16.0	−149	−1220	359.2
20	−22.7	−31.8	− 29.4	−19.5	−180	−1249	339.7
21	−25.6	−24.4	− 19.2	−16.8	−205	−1268	322.9
22	−28.7	−30.8	− 15.2	−19.3	−235	−1283	303.6
23	−32.2	−27.4	− 17.2	−18.0	−263	−1300	285.6
24	−35.3	−28.4	− 15.1	−17.2	−291	−1316	268.4
					±9.6	0	

Tables II to VI contain the data from which were plotted the curves of Figs. 5 to 11 respectively.

TABLE II. *Data for curves of Figure 7.*

Step	Field Current I (Amps.)	ΔH	ΔJ	Observed ΔT in mm	H	J	Total change in T(mm)
Steps	1 to 12 are the same as in Table I.						
13	1.9	13.2	219	35	6.6	766	169.6
14	4.0	15.4	196	60	22.0	962	230
15	7.9	33.4	130	18	55.4	1092	248
16	11.9	33.4	62	−15	88.8	1154	233
17	15.1	26.2	34	−20	115.0	1188	213
18	18.9	32.5	34	−28	147.5	1222	185
19	22.7	31.7	26	−28	179.2	1248	157
20	25.5	24.2	18	−19	203.4	1266	138
21	29.1	32.3	18	−23	235.7	1284	115
22	32.3	27.5	16	−20	263.2	1302	95
23	35.3	29.3	14	−20	292.5	1316	75

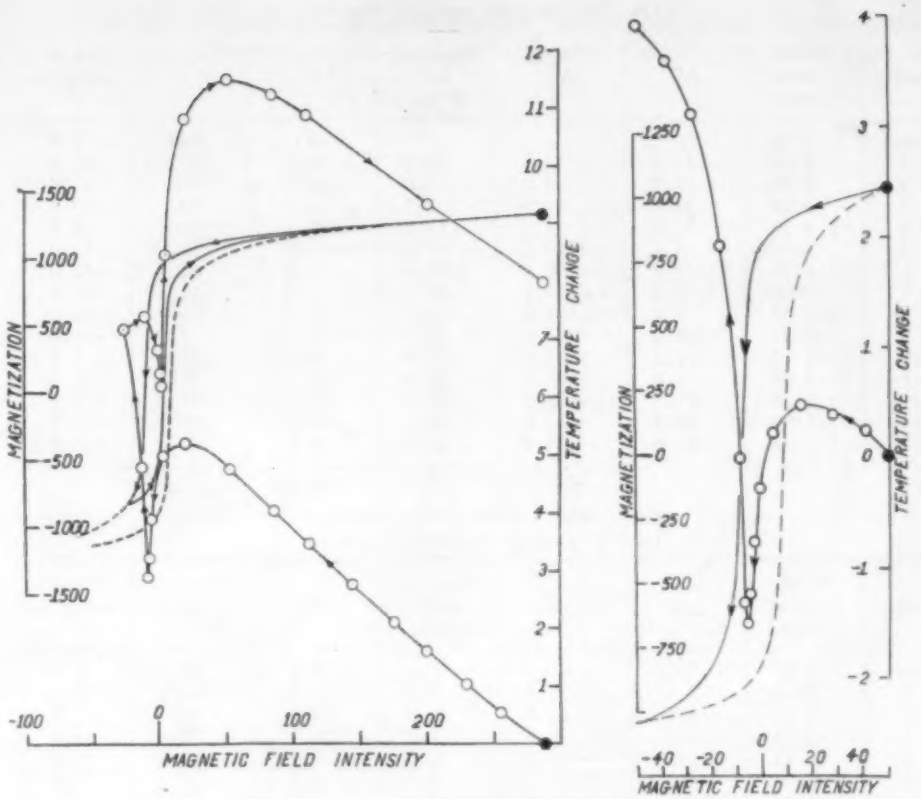


Fig. 8. The magneto-thermal relations associated with an asymmetric hysteresis loop formed between $H=-25$ and $H=290$ gauss.

Fig. 9. The magneto-thermal relations associated with the medium sized hysteresis loop.

TABLE III. *Data for curves of Figure 8.*

Step	Field Current I (Amps.)	ΔH	ΔJ	Observed ΔT in mm	H	J	Total change in T(mm)
Steps	1 to 15 are the same as in Table I.						
16	−1.9	15.8	88.1	10	−9.2	−737	315
17	−0.5	9.4	182	−25.5	0.2	−555	290
18	−0.0	1.8	137	−17.5	2.1	−418	272
19	0.5	1.1	223	− 9.5	3.2	−195	263
20	1.9	3.6	794	98.5	6.8	599	361
21	4.0	13.8	336	99.5	20.6	935	461
22	8.0	32.5	149	30.0	53.1	1084	491
23	12.0	33.7	65	−11.5	86.5	1149	479
24	15.1	26.2	35	−16.0	112.9	1184	463
25	25.9	90.7	81	−65.5	203.7	1265	398
26	36.1	89.5	51	−59.5	293.2	1316	338

TABLE IV. *Data for curves of Figure 9.*

Step	Field Current (Amps.)	ΔH	ΔJ	Observed ΔT in mm	H	J	Total change in T
Start	7.21				49	1044	0.0
1	5.87	−11.2	− 23.3	10.0	39.7	1021	10.0
2	4.56	−10.9	− 28.0	6.0	26.8	993	16.0
3	3.08	−12.5	− 46.9	3.5	14.3	946	19.5
4	1.62	−11.0	− 85.4	−11.0	3.3	860	8.5
5	0.83	− 5.1	−116.2	−21.5	− 1.8	744	−13.0
6	0.39	− 2.2	− 96.8	−21.0	− 4.0	648	−34.0
7	0.00	− 1.5	−129.7	−20.5	− 5.5	518	−54.5
8	−0.39	− 1.1	−184.0	−11.5	− 6.6	334	−66.0
9	−0.83	− 0.9	−262.0	8.0	− 7.7	72	−58.0
10	−1.62	− 2.2	−445.0	56.5	− 9.9	−373	− 1.5
11	−3.08	− 7.8	−394.0	83.0	−17.7	−767	81.5
12	−4.58	−11.5	−158.0	51.0	−28.8	−925	139.5
13	−5.90	−10.4	− 73.4	21.0	−39.2	−998	153.5
14	−7.25	−11.0	− 45.9	14.0	−50.2	−1044	167.5
					±8.1	0	

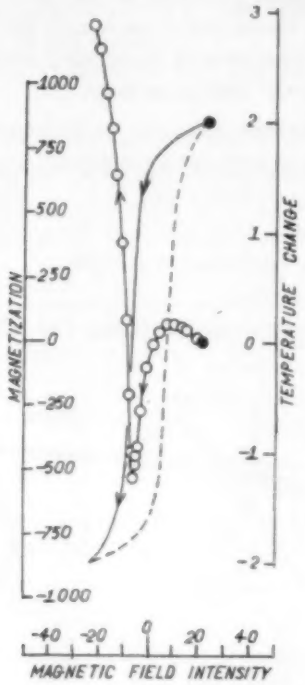
TABLE V. *Data for curves of Figure 10.*

Step	Field Current (Amps.)	ΔH	ΔJ	Observed ΔT in mm.	H	J	Total change in T
Start	3.80				21.1	857	0.0
1	3.50	−2.5	− 9.4	2.0	18.5	847	2.0
2	3.05	−3.6	− 15.9	3.0	14.9	831	5.0
3	2.78	−2.2	− 10.9	1.0	12.7	820	6.0
4	2.42	−2.8	− 16.5	1.0	9.9	804	7.0
5	2.02	−3.0	− 21.7	0.0	6.9	782	7.0
6	1.63	−2.9	− 29.4	− 3.0	4.0	753	4.0
7	1.23	−2.7	− 39.3	− 5.0	1.3	714	− 1.0
8	0.83	−2.4	− 57.6	− 9.0	− 1.1	656	−10.0
9	0.39	−2.4	− 95.0	−17.0	− 3.5	561	−27.0
10	0.10	−1.3	− 90.6	−14.0	− 4.8	470	−41.0
11	0.00	−0.4	− 34.1	− 3.5	− 5.2	436	−44.5
12	−0.10	−0.3	− 36.6	− 3.5	− 5.5	399	−48.0
13	−0.39	−0.8	−144.1	− 5.0	− 6.3	255	−53.0
14	−0.83	−0.8	−260.0	+10.0	− 7.1	− 4	−43.0
15	−1.24	−1.0	−235.5	22.5	− 8.1	−240	−20.5
16	−1.63	−1.3	−194.1	29.0	− 9.4	−434	8.5
17	−2.03	−1.9	−142.7	30.0	−11.3	−577	38.5
18	−2.42	−2.2	− 96.4	26.5	−13.5	−673	65.0
19	−2.81	−2.3	− 63.9	18.0	−15.7	−737	83.0
20	−3.07	−1.8	− 38.4	14.0	−17.6	−775	97.0
21	−3.51	−3.3	− 52.0	17.0	−20.9	−827	114.0
22	−3.81	−2.2	− 29.3	9.5	−23.1	−857	123.5

TABLE VI. *Data for curves of Figure 11.*

Step	Field Current (Amps.)	ΔH	ΔJ	Observed ΔT in mm.	H	J	Total change in T
Steps	1 to 11 are the same as in Table V						
12	0.40	−2.8	− 25.4	1	− 1.8	461	−43.5
13	0.84	−3.1	− 26.2	3.5	1.3	487	−40.0
14	1.64	−5.5	− 87.6	14.0	6.8	575	−26.0
15	2.80	−7.8	−139.5	32.5	14.6	715	6.5
16	3.82	−7.7	− 83.3	23.0	22.3	798	29.5

The three magnetic cycles which were investigated are shown together in Fig. 13. The results obtained are indicated roughly by the broken lines



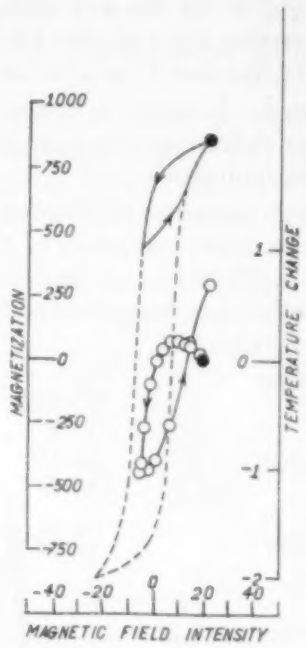


Fig. 10. The magneto-thermal relations associated with the smallest hysteresis loop studied.

Fig. 11. The magneto-thermal relations associated with an asymmetric loop formed between $H=22$ gauss, and zero impressed field.

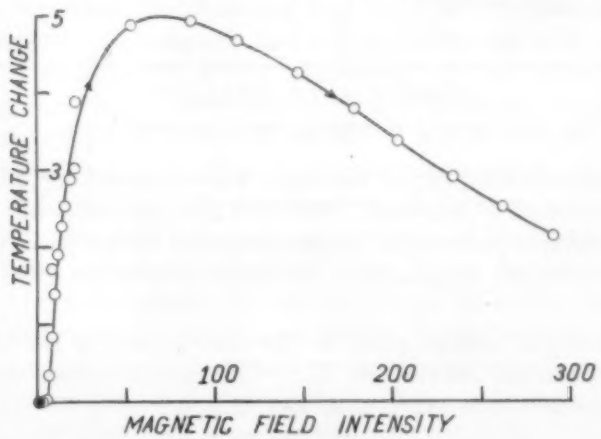


Fig. 12. The magneto-thermal phenomena of the "virgin curve."

L and L'. The intersection of these lines with the loops correspond to the successive maxima and minima of the *temperature-magnetic field intensity*

curves. If one is traversing *any* magnetic path in the direction of decreasing magnetic field intensity, and if one views the line L in the direction indicated by the arrow, then cooling is observed along those portions of the path which lie to the right of the line and heating along those portions which lie to the left. In traversing *any* magnetic path in the direction of increasing magnetic field intensity, the line L' is to be used in exactly the same way.

(c). **Energy**. In order to convert temperature changes as indicated by galvanometer deflections into heat developed in ergs it is necessary to know the following quantities:

1. The galvanometer calibration constant,
2. The thermoelectric power of the copper constantan couple,
3. The specific heat and the density of the iron,
4. The effect of the solder and the thermocouples upon the thermal capacity of the iron.

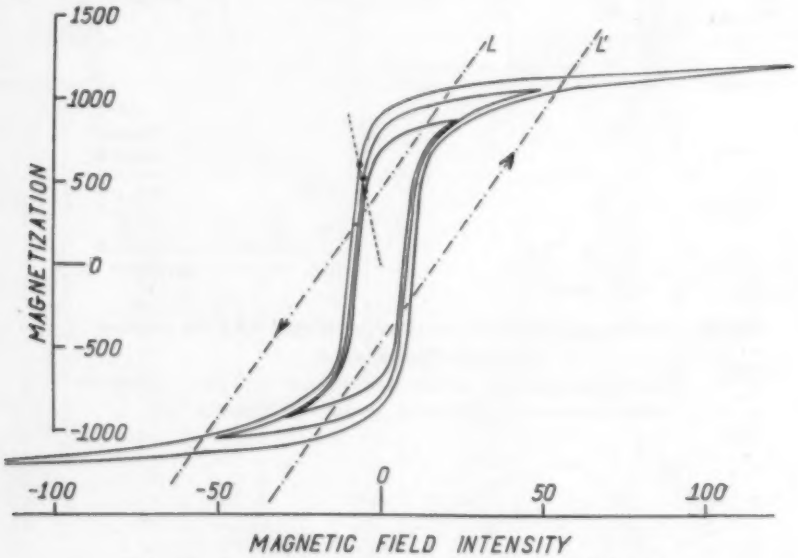


Fig. 13. Summary of observations on hysteresis heats.

The galvanometer calibration constant was obtained by means of the potentiometer heretofore described. It is 103 mm per microvolt.

The thermoelectric power of a couple composed of the wires used in this experiment was carefully measured. For a single couple it is 41.75 microvolts per degree C.

The value which is here adopted for the specific heat of the steel used in this research is 0.116 gm calories per °C.[10] This quantity was not measured. The measured density of the steel used is 7.75 g/cc.

[10] The International Critical Tables page 118, Vol. V, give the specific heat of steel in terms of the temperature and the carbon content. Between 0 and 100° C the specific heat in joules per gram is $0.4661+0.0184 \times$ (% carbon). Taking 4.18 joules per calorie the specific heat for 1.08% carbon steel is 0.116 which is the value used here. Other authorities give values ranging from 0.098 to 0.118 but are not explicit as to the kind of steel described.

The thermal capacity of the solder and thermocouple wires is assumed to be that of a sheath of solder 0.005 cm thick surrounding each bar. This introduces an additive correction of 3% to the calculated energies. The temperatures given in the Tables I to VII have not been corrected for the effect of the solder.

The results of the energy calculations are presented in the following table.

The iron, being initially in a cyclic state, is carried through a half cycle of magnetization by diminishing H in successive steps of varying magnitude. Column 2 of Table VIII gives the number of such steps and therefore an indication of the manner of performance of the half cycle. Column 3 con-

TABLE VIII.

Cycle	No. steps per half cycle	Heat developed per half cycle (ergs)	
		from thermal obs.	from hysteresis loop
Largest	1	28 800	29 000
	2	27 750	
	4	27 150	
	14	23 300	
	24	23 400	
Medium	1	15 300	17 000
	14	14 600	
Small	1	9 950	11 500
	22	10 800	

tains the observed total heats developed, corrected for the effect of the solder. Column 4 gives the half area of the three hysteresis loops expressed in ergs.

Too much significance should not be attached to a comparison of the energy values given in columns 3 and 4. The combined cumulative error inherent in both the magnetic and thermal measurements must be expected to appear in such a comparison. However, the interesting result here definitely exhibited, is the fact that the heat developed in the large cycle of magnetization depends upon the manner in which the cycle is performed.

It appears that in a cycle of magnetization which saturates, or nearly saturates, the iron the heat developed during a slow traversal of the cycle is appreciably less than that given by the area of the hysteresis loop, though the latter also represents magnetic data taken during a slow traversal.

If one views the possibility of the storage of energy in the iron in the form of magnetostrictive strain as well as in the form of heat, then one is lead to the conclusion that a slow cycle of magnetization which leaves the iron in the same magnetic state should, for the case under review, leave the iron with a permanent or semi-permanent elongation. This effect should be absent if the cycle be traversed rapidly. This phenomena has been observed elsewhere[11] and is now the subject of further investigation in this laboratory.

[11] S. R. Williams, Phys. Rev. **34**, 258 (1912), also see Ewing, 1st. Ed. p. 74 also p. 327.

E. Sources of Error and Precision of Measurement

(a). **Magnetic measurements**. The uncertainty in the absolute value of H varies for the different magnetic paths but in no case amounts to more than 3%. As regards J, the larger paths could be repeated to 1% while for the smaller paths the uncertainty may be as large as 5%. In general the reproducibility of the magnetic data indicates a precision of 5% or better in the determination of ΔH and ΔJ.

The uniformity of the magnetic field throughout the test specimen is examined as follows:— The inner group of 51 thermocouples is connected in series opposing the outer group of 51 thermocouples, and the magnetization is reversed from maximum to maximum producing a deflection of 7 mm. If the 102 thermocouples had been connected in series aiding, the heat developed by the process would have produced a galvanometer deflection of 330 mm. The observed deflection of 7 mm indicates that the magnetic field is uniform to 2% over the cross-section of the ellipsoid.

A further check on the magnetic behavior of the aggregate of bars is obtained as follows:—Consider a typical H–J hysteresis loop. If now a line be drawn through the origin and through the point on the loop corresponding to the zero value of magnetizing current in the solenoid, (e. g. the dotted line in Fig. 13), then the tangent of the angle between this line and the J axis is the so called "demagnetizing factor" of the specimen. This follows immediately on setting $H_0 = 0$ in the expression

$$H = H_0 - NJ,$$

in which, H_0 = the field of the magnetizing current, and N = demagnetization factor or form factor. Values of N for the ellipsoid determined in this manner from the three hysteresis loops agree to 5% and exhibit no systematic variation.

(b). **Thermal measurements**. Since the thermal measurements may be repeated to the limit of accuracy stated above, any sources of error appearing therein must be systematic. Sources of systematic error considered are the following:

1. The radiation correction,
2. Eddy currents,
3. Time lag in magnetization,
4. Effect of magnetic field on the thermoelectric power.

1. *Radiation correction*. The logarithmic decay of the thermocouple *emf* is slightly different for each observation. This is due to a change in temperature of the rice flour environment of the iron bars, and a change in temperature of the copper bars, resulting from preceding operations. As has been stated, the extrapolation to zero time is performed for every observation. The validity of the method of extrapolation is established over the experimental range of the temperature changes both for heating and cooling in the following manner:

An *emf* equal and opposite to the sum of the extrapolated *emf* and the steady switch parasitic *emf* is inserted in the thermocouple circuit by means of the potentiometer R, r, of Fig. 5. The desired temperature change is then effected and the galvanometer is immediately connected to the thermocouple potentiometer circuit. The correctness of the extrapolated thermal *emf* is indicated by an initial zero galvanometer deflection.

2. *Eddy currents.* An estimate of the eddy current loss in the cylindrical bars may be obtained from the following formula,[12]

$$Q = (\Delta B)^2 \times \frac{\lambda R^2}{8t},$$

in which Q = heat per unit volume in ergs, R = radius of a single bar, λ = electrical conductivity of the material, t = time required to establish the change ΔB, and $\Delta B = \Delta H + 4\pi\Delta J$.

In the derivation of this formula it is assumed that ΔB varies linearly with ΔH and that ΔH varies linearly with the time. An oscillogram of the increasing current in the solenoid indicates that t is of the order of 0.01 second, assuming that H and J follow in time the impressed magnetizing field. It follows that the heat due to eddy currents in the iron is a negligible factor in this experiment. The same applies to the heat due to eddy currents in the copper bars except on those portions of the hysteresis loop over which the change in J is smaller than the corresponding change in H. There calculation shows that the eddy current heat in the copper may be of the same order of magnitude as that in the iron, though not of the same order as the cooling actually observed. The following experiment proves that there is no measurable difference between the eddy current heat developed in the copper and the iron in this portion of the loop. A reduction of the field from +290 to +150 gauss causes a heating of the iron, while an increase of the field from +150 to +290 gauss produces an equal cooling. Thus, if this loop be traversed very rapidly there is no net change in temperature of the iron. The fact that one side of this loop is thermally equal and opposite in sign from the other side shows that in this region the effects of eddy currents are quite inappreciable.

3. *Time lag in magnetization.* It will be observed on reference to Fig. 5 that the flux from 59 iron bars links the thermocouple circuit. Accordingly any time lag in magnetization would induce uncompensated electromotive forces in this circuit after the galvanometer is connected therein. The absence of any such effect is established by connecting the 48 turn coil to a highly sensitive ballistic galvanometer immediately after the reversal of the maximum magnetizing field. No deflection is observed.

4. *Effect of magnetic field on thermoelectric power.* The thermoelectric power of a couple composed of the wires used in this experiment was found to be unaffected by a strong magnetic field.

[12] U. Adelsberger, Ann. d. Physik [4] **83,** 199 (1927).
[13] U. Adelsberger, Ann. d. Physik [4] **83,** 184 (1927).

F. Remarks

The problem of the present paper has recently been attacked by Adelsberger,[13] F. W. Constant,[14] and Honda, Okubo, and Hirone.[15] The several experimental methods devised by these investigators were not so elaborate as the present method. None of them report any of the cooling effects characteristic of the curves submitted above. Adelsberger worked with tungsten steel and a special Krupp steel and Constant with K. S. magnet steel. Since it is not definitely known that the cooling takes place in any other material than carbon steel of the sort used in this experment, Honda's results for carbon steel are the only ones which offer any definite basis for comparison. The sensitivity of Honda's apparatus, as given by Table II of this paper, was 14.5 mm per 100,000 ergs of heat developed, which is to be compared with 1150 mm per 100,000 ergs for the present method. This, together with the method of observation adopted by Honda and his collaborators, may account for their failure to observe the cooling effects. However, since Honda's steel contained only 0.2% carbon, and since the cooling effects noted in our 1.08% carbon steel differ markedly in magnitude from those in our 1.35% carbon steel, the evidence is not conclusive that the cooling effects are a general property of steels. Further experiments bearing on this point are now in progress.

In conclusion I wish to acknowledge my indebtedness to those without whose cooperation this work could not have been accomplished; in particular to Dr. William Campbell who made the microphotographic analysis and to Dr. Harold Fales who made the chemical analysis of the steels; to Dr. Walter P. White for advice on the thermocouple assembly and manipulation; and to Dr. S. L. Quimby who suggested the problem and followed its progress with helpful counsel and encouragement.

[14] F. W. Constant, Phys. Rev. **32**, 486 (1928).
[15] Honda, Okubo, and Hirone, Sci. Rep. of the Tohoku Imp. Univ. [I] **18**, 409 (1929).

A NEW METHOD OF MEASURING THE VARIATION OF THE SPECIFIC HEATS (c_p) OF GASES WITH PRESSURE

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Abstract

A method is described whereby the ratio of c_p at a high pressure to c_p for the same gas at a pressure of one atmosphere taken as a standard is determined. The continuous flow principle is used in such a way that the necessity for measuring gas flow and heat input is avoided. A stream of gas at high pressure is brought to a temperature t_1 and passed through a heat interchanger acquiring there a temperature t_2, after which it is throttled to atmospheric pressure, brought to a temperature t_3 and returned to the heat interchanger, where its temperature again becomes t_2. The ratio of c_p at a high pressure to that at atmospheric pressure is equal then to $(t_3-t_2)/(t_2-t_1)$ plus certain small corrections. Measurements on commercial oxygen taken at a mean temperature of 26° C and pressures ranging from 15 to 100 atmospheres indicate a pressure coefficient of this ratio of 0.00165 ± 0.00005 per atmosphere.

IN CONSIDERATION of the need for further data on the specific heats of gases the present work was undertaken with the object of developing a method of determining the variation of c_p with pressure for a number of gases over a large range of pressure and temperature. Air[1,2] and ammonia[3] are the only gases on which direct measurements on c_p have been made over a considerable range of pressure. Indirect determinations follow from data on the Joule-Thomson effect. Here we note the work of Burnett[4] on CO_2 and Roebuck[5] on air. Recently Beattie[6] and Bridgeman[7] using the Beattie-Bridgeman equation of state have calculated c_p as a function of pressure and temperature for air and ammonia.*

The method of measurement to be described in this paper is of value because of its simplicity and the fact that the usual calorimetric errors are easily detected and in most cases eliminated. It possesses the advantage of avoiding the measurement of quantities of matter and of energy. On the other hand relative values only are determined.

A schematic arrangement of the apparatus is shown in Fig. 1. B and B' are constant temperature baths and I is a heat interchanger. The gas at high

[1] Lussana, Nuov. Cim. 1894 to 1908.
[2] Holborn and Jacob, Berl. Ber. **1**, 213 (1914); also Zeit. Inst. **31**, 116 (1911).
[3] Osborne, Stimson, Sligh and Cragoe, Sci. Papers Bureau of Standards **20**, 65 (1924).
[4] Burnett, Phys. Rev. **22**, 590 (1923).
[5] Roebuck, Proc. Amer. Acad. Arts and Sciences **60**, 537 (1925).
[6] Beattie, Phys. Rev. **34**, 1615, (1929).
[7] Bridgeman, Phys. Rev. **34**, 527, (1929).

* For a review of the earlier work on this subject, see Partington and Shilling, "Specific Heats of Gases," London, 1924.

pressure passes through the tube a in the bath B where it comes to a fixed temperature. It then passes through the interchanger where its temperatures on entering and leaving are measured. After leaving the interchanger the pressure is reduced almost to one atmosphere by the reduction valve V. It now passes through a second constant temperature bath B', back through the interchanger, and escapes. The temperatures at entrance and exit are measured as before.

The interchanger is so constructed that the two gas streams, after passing through a region where their entrance temperature are measured, are brought into such intimate thermal contact that they leave the interchanger at approximately the same temperature.

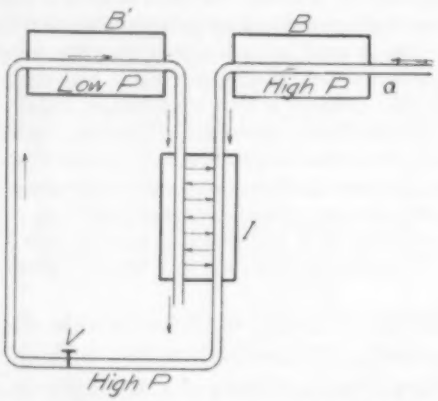

Fig. 1. Schematic arrangement of apparatus.

If there is no net passage of heat from the interchanger to the surroundings, then the amount of heat gained by one stream is equal to that lost by the other. Further, since these streams are equal, it follows that the ratio of the two specific heats are inversely as the temperature changes in their respective lines; i.e. $(c_p)/(c_p)_0 = (t_3 - t_2)/(t_2 - t_1)$†. Methods of applying small corrections to values thus obtained will be discussed later.

During the course of this work three different types of interchangers were constructed and used. The third and best will be described in detail. Fig. 2 shows a sectional drawing of the third interchanger. For convenience it is made schematic to the extent that only one gas line (low pressure) is shown entering and leaving. Except for a smaller diameter and a greater wall thickness the construction of the high pressure line where it enters and leaves is the same. In general the heavy lines represent polished copper an the light lines German silver, thinly copper-plated. The low pressure gas enters at a from the bath, its line of flow being protected by the heavy copper shield S_1 which is thermally coupled to the bath and the tube a within the bath.

† Recently attention has been directed to the work of Callendar (Roy. Soc. Phil. Trans. **212**, 1 (1912) and of Romberg Amer. Acad. Proc. **57**, 377–387 (1912) where the variation with temperature of the specific heat of water was determined by a similar method of flow calorimetry.

At *b* the gas is stirred by a small tuft of steel wool and passes along the thermometer tube *c* where it is further stirred in its path by small fins soldered to *c* (not shown).

At *d* the gas passes out through a copper tube which bends back sharply (not shown in drawing) and passes to *e* along the length of the shield S_2, to which it is soldered for thermal contact. The section *gg'* is interposed between the thermometer cell and the point *g* beyond which interchange begins, in order to minimize errors arising from heat conduction. Both this section and the corresponding section *uu'* of the high pressure line pass parallel to each other in a dead air space bounded by the tube *f*.

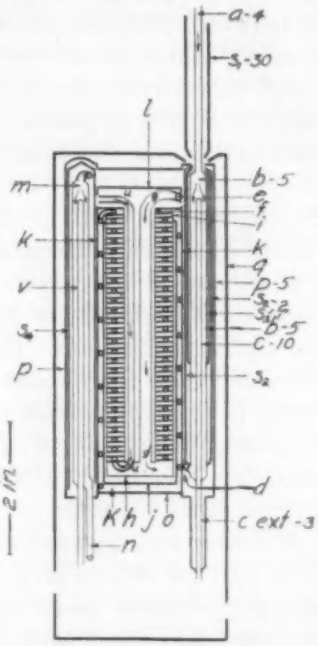

Fig. 2. Sectional drawing of interchanger. Copper in heavy lines, German silver in light lines. Letters refer to text; numbers indicate thickness of the walls in thousandths of an inch.

About the tube *f* are two thin copper ribbons wound helically and spaced as shown. To these are tin soldered the high pressure line shown by the small circles. Fitting snugly over this helical ribbon is a cylinder *h* closed at lower end. The two gas streams are therefore constrained to spiral around an axis (twenty-four times) in passing from *g'* to *i*, both being closely coupled thermally.

The cylinder *h* above referred to has a double wall, the outside of which *j* is of copper with an intervening dead air space. The high pressure line is wound on the outside of the cup as shown, soldered in place, and closed over with a thin copper cylinder *k* which makes a tight enclosure and extends across the upper end to provide the shield *l*. The two gas streams flow around seven or eight times before reaching the end chamber *K*. From *k* the low pressure gas enters a copper tube, which is soldered, as in the case of the inlet

tube, to a shield S_4 and leads to the tube m which is exactly similar in size and arrangement to the inlet tube b. The gas leaves by way of the tube n (shown in part) and passes out into the room.

After the interchange of heat and before the exit temperatures are measured, both exit streams are put in good and approximately equal thermal contact with the end plate o as a means of making a base for the external shield p which surrounds the interchanger and provides it with an equal temperature boundary. A heavy copper cylinder q provided with a heating coil acts as a heater guard and is kept at the same temperature as the surface of the interchanger. This is accomplished by adjusting the heater current to maintain a zero reading on a five-junction copper-constantan thermocouple connected differentially between the constant temperature boundary (near its base) and the inside of the heater guard.

The thermal capacity of the interchanger, including the four thermometer tubes is equivalent to approximately 18 grams of water and requires on the average about 35 minutes to attain a steady state with a flow of 50 cc/sec. at atmospheric pressure.

The two baths are exactly similar, each consisting of an outer bath which contained an electric heating coil and thermostat as well as a large coil through which the gas flows, and an inner bath without heating or cooling coils which served to smooth out temperature fluctuations due to the heater current in the outer bath which surrounds it. The bath liquid was kerosene. The similarity of the baths and their thermostat mountings made it possible quickly to reverse the order of the bath temperatures.

All temperature measurements were made with copper-constantan, thermocouples, used differentially. The tubes c and v (Fig. 2) were provided for the insertion of a five-junction thermocouple to read the temperature change in the low pressure line. A similar arrangement was used for the high pressure line. In addition, for the purpose of checking, a two-junction couple was provided for the two inlet temperatures and a similar one for the two outlet temperatures. Only the copper lead wires were permitted outside the heater guard. Potential differences were measured with a White single potentiometer using the usual auxiliary equipment.

The similarity of the thermoelectric properties of the thermocouples was established by standardization and the formula of Adams[8] was used in obtaining the temperature intervals from the bridge readings in microvolts.

Pressure readings were taken on a spring gauge, devised by combining an optical indicating arrangement (telescope, mirror and sale) with a high class Bourdon spring of the type used in hydraulic gauges. This arrangement gave approximately 530 scale divisions for a pressure of 100 kg/cm^2. The gauge was calibrated against a Pratt and Whitney dead-weight gauge.

Commercial oxygen gas (water free) with a flow of approximately 50 cc/sec. was used. Two cylinders connected in parallel provided a reservoir sufficiently large to permit the taking of temperature and pressure readings continuously, thus eliminating the necessity of pressure control on the high

[8] Adams, J. Wash. Acad. **3**, 469 (1913).

pressure side. The flow of gas was controlled from the low pressure side by adjusting an ordinary pressure reduction valve in such a way as to maintain a constant pressure (11 pounds/sq. in.) on a glass capillary leak.

The bath temperatures were controlled by mercury-in-glass thermostats so as to maintain one gas inlet stream at approximately 33.2°C and the other at approximately 18.8°C.

In making a run the baths were brought to steady state of temperature regulation and the gas started through the interchanger. The heater guard temperature was then adjusted until it was the same as the surface of the interchanger. After the steady state had been reached a zero reading on the heater guard thermocouple was maintained for about 15 minutes before taking calorimetric measurements. In regulating the guard temperature the observer also gave attention to the room temperature. It was thought desirable that the room temperature should be kept fairly constant with respect to the outside temperature of the interchanger, which differed from the arithmetic mean of the bath temperatures depending upon the pressure of the high pressure gas and the order of the bath temperatures. This was accomplished by keeping the room temperature such that the heater guard temperature could be regulated by limiting its power input to the small range 0 to 0.35 watt. After the heater guard thermocouple had indicated zero for 15 to 20 minutes, readings were taken on the pressure gauge and the four thermocouples. From two to four sets of readings were taken in a given pressure range. The bath thermostats were then interchanged thus reversing the order of the bath temperatures and another group of readings taken at a somewhat lower pressure.

Let the subscript 1 be applied to the state of the high pressure gas upon entering the interchanger and the subscript 2, to that upon leaving. Similarly let the subscripts 3 and 4 apply to the low pressure line entering and leaving respectively. Further, let i stand for the function $u+pv$. Now if q is the heat from various outside sources gained per gram for both streams, we have

$$q = i_2 - i_1 + i_4 - i_3. \tag{1}$$

Now it is reasonable to assume that the variation of these functions is linear over the small range of temperature and pressure in each gas line. We then get

$$q = c_p[T_2 - T_1 + \mu(p_1 - p_2)] + (c_p)_0[T_4 - T_3 + \mu_0(p_3 - p_4)] \tag{2}$$

where the subscript 0 applies to conditions at atmospheric pressure and μ is the Joule-Thomson coefficient. It finally follows that

$$\frac{c_p}{(c_p)_0} = -\frac{T_4 - T_3 + \mu_0(p_3 - p_4)}{T_2 - T_1 + \mu(p_1 - p_2)} + \frac{q}{(c_p)_0[T_2 - T_1 + \mu(p_1 - p_1)]} \tag{3}$$

Since we measure $(T_4 - T_3)/(T_1 - T_2)$ we write Eq. (3) in the form:

$$\frac{T_4 - T_3}{T_1 - T_2} = \frac{c_p}{(c_p)_0} + \phi(\mu, q) \tag{4}$$

where $\phi(\mu, q)$ is a correction term. The sign of this term is changed, but not its value if we interchange the bath temperatures; so that these corrections can be eliminated. The whole problem thus centers on the accurate measurement of the various temperatures. With an ideal interchanger in which pressure drops and thermal leakages are negligible we see from what has been said before that the last term in Eq. (4) would vanish.

The mean values of the ratio on the left of Eq. (4) for each group of readings were calculated and they are shown plotted against the corresponding mean pressures in Fig. 3. Curve 1 represents values obtained when the high pressure bath was maintained at 33.2°C and the low pressure bath at 18.8°C; while curve 2 gives the values obtained with the reverse order of bath temperatures. The fact that curves 1 and 2 do not coincide and pass through

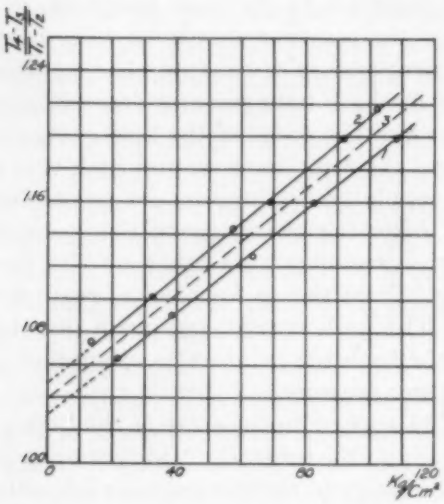

Fig. 3.

the point $p = 1$ atmosphere and $(t_4 - t_3)/(t_1 - t_2) = 1$ gives evidence that we are not dealing with the ideal calorimeter just referred to.

In order that the difficulties might have further study a set of observations was taken with both baths set at 26°C and a flow of 50 cc/sec. A cooling effect in each gas stream as it passes through the interchanger was observed. The magnitude of the effect for three different pressure regions is shown in Table I.

If corrections of the type given in the last column of Table I were to be applied along the length of the two curves the general effect would be to change the shape of each slightly and bring them somewhat closer together. Since the proposed corrections would not affect in any sense the mean curve 3 of 1 and 2 they are not applied. These corrections include the Joule-Thomson effect, velocity cooling and possible index errors; and we conclude that the mean curve is independent of the Joule-Thomson effect and heat leakage q.

A part of the separation between curves 1 and 2 might be attributed to

temperature effects upon the specific heat c_p of oxygen. Since there is considerable evidence to show that c_p at atmospheric pressure changes very slightly with temperature in the region in which we are interested, we shall consider it as constant. On the other hand, c_p at pressures of 60 and 100 kg/cm² decreases quite considerably with temperature increase between 0 and 50°C. Data of this type on oxygen are lacking but if we adopt values calculated by Beattie[6] or by Bridgeman[7] for air and make corrections to curves 1 and 2, assuming air and O_2 to be alike in these respects, we find that the correction is more than sufficient to bring them together at 100 kg/cm² pressure. If, on the other hand, we use observed values quoted by Beattie,

TABLE I

High pressure kg/cm²	High Pressure line cooling °C	Low Pressure line cooling °C	Calculated correction factor for corresponding points on 1 and 2, Fig. 3.
13	0.023	0.020	Curve 1 1.008 Curve 2 0.992
64	0.008	0.008	Curve 1 1.002 Curve 2 0.998
83	0.015	0.012	Curve 1 1.003 Curve 2 0.997

the corrections so obtained are not sufficient to reduce the divergence between 1 and 2 at 100 kg/cm² by more than 50 percent. If we make similar corrections at lower pressures, 0 to 20 kg/cm², it is seen that the effect almost vanishes. It should be observed, however, that the corrections listed in Table I for this region are almost sufficient to bring the two curves together.

It is apparent therefore, that uncorrected curves obtained in the manner that 1 and 2 were obtained will never coincide for the large temperature intervals here used and may have slopes such that the divergence between them will increase slightly with increases in pressure. It is equally apparent however, that we are justified in drawing a mean curve 3.

The residual errors giving the effect of moving the mean curve 3 upward by approximately 4 percent must be due to difficulties in measuring temperature changes in one of the thermometer tubes. The difficulty doubtless lies in the fact that heat is conducted along the high pressure entrance thermometer tube. An examination of the entrance thermometers in the interchanger gives evidence of the possibility of some interchange of heat between the two gas streams before the temperatures are determined. The effect of this is to induce a temperature gradient in the thermometer cells and therefore an uncertainty in meaning of the temperature readings. The results indicate that this effect is larger in the case of the high pressure line as might be expected from the construction. It also appears in this connection that errors of this type depend only on the general temperature distribution in the apparatus to a high degree of approximation. The slopes of the curves in Fig. 3, therefore, are not affected appreciably. It is of especial interest to note that

with the first (and very faulty) apparatus curves were obtained intersecting the horizontal axis at about 30 kg/cm² having, however, appproximately the same slope as the mean curve here given.

The apparatus was designed to work in the region from 20 to 200 atmospheres and therefore too much confidence should not be placed in measurements taken at pressures lower than 20 atmospheres.

The mean value of the slope between 30 and 100 kg/cm² is 0.00160 per unit of pressure here used, or 0.00165 per atmosphere. The value obtained from the first apparatus mentioned above is 0.00176 per atmosphere and that from a second apparatus is 0.00171 per atmosphere. The two earlier sets of apparatus, moreover, embodied a radically different method of measuring temperatures, namely that the thermometer tubes and their respective shields for measuring t_1 and t_1 were located in the baths B and B' (Fig. 1).

Although the present work has been done on oxygen, it is not without interest to compare results with those already obtained for air. The experimental work of Roebuck gives 0.00140 per atmosphere, while the calculations of Beattie from the Beattie-Bridgeman equation of state yield, 0.00166 per atmosphere. The experiments of Holborn and Jacob while performed at 59°C (where the value 0.00119 emerges) may be reduced to the temperatures of these experiments by using the calculations of Beattie, resulting in the value 0.00162 per atmosphere.

The agreement in the values for $(d/dp)\ [c_p/(c_p)_0]$ as obtained by the use of three calorimeters is considered sufficient evidence for establishing the validity of the method for precise work. This point could be made more impressive if space could be taken to describe in detail the great differences in type and quality of the three sets of apparatus. The arrangement of the apparatus last used possesses many defects, many of which can be almost completely eliminated by more careful design and construction. Perhaps the most important feature of the method over and above its simplicity is the fact that the sources of error speak their presence in the nature of the results which it yields.

Plans to investigate gases other than oxygen and to extend the readings over a range of temperature were brought to a halt by the development of a leak in the interchanger. This, together with the fact that designs for an improved apparatus were in mind, made it seem wiser to publish the results already obtained and defer the general survey until the new designs could be realized.

In conclusion the author wishes to express thanks to Professor L. G. Hoxton who proposed the method for his interest during the progress of the work.

NOTE ON THE PRESSURE VARIATION OF SPECIFIC HEATS OF GASES DERIVED FROM COMPRESSIBILITY DATA

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University of Virginia

(Received August 7, 1930)

Abstract

Values of the rate of variation of c_p with pressure at constant temperature as calculated from p-v-T data and as determined by direct experiment are compared for oxygen and air over a pressure range of 20 to 100 atmospheres and at 26° C. The calculated values, while of the same order of magnitude as the experimental, are shown to be very sensitive to small variations in the coefficients of the "equation of state" employed; also to modifications in the method of approximation used in handling such equations. The conclusion is reached that this rate probably diminishes slowly with rising pressure for oxygen in the field considered and that its calculated values cannot at present approach in accuracy what may reasonably be expected from direct calorimetric experiments.

THE computation of thermodynamic properties of gases from p-v-T data has recently been brought forward by Beattie and Bridgeman who have developed an "equation of state"[1] and have applied it with surprising success to the evaluation of the Joule-Thomson effect and the heat capacity at constant pressure (c_p) for air.[2,3,4] Also a new method for the experimental determination of the relative values of c_p at different pressures and the same temperature is reported elsewhere in this issue by E. J. Workman. It would seem of interest, therefore, to compare the result there given for oxygen with calculated values and, if possible, to draw conclusions as to the applicability of computations of this nature.

Since the thermodynamic relation essential in this connection, namely

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{1}$$

involves, in effect, the curvature of a graph adjusted to experimentally determined points, often far apart, one is led to expect that a large variety of values for the curvature are possible depending upon the form of the equation employed and upon the number of points; further, that any equation of state which is adjusted to fit over a wide range of data, which is its usual purpose, may not be so suitable as an interpolation formula utilizing

[1] J. A. Beattie and O. C. Bridgeman, Jour. Am. Chem. Soc. **50**, 3133 (1928); also Zeits. f Physik **62**, 95 (1930).
[2] O. C. Bridgeman, Phys. Rev. **34**, 527 (1929).
[3] J. A. Beattie, Phys. Rev. **34**, 1615 (1929).
[4] J. A. Beattie, Phys. Rev. **35**, 643 (1930).

closer points merely. An ideal case, in fact, would be the one where the points are so closely distributed that interpolation by successive differences alone might be used.

In what follows calculated values of the same quantity for oxygen will be compared among themselves and with experiment, with a view to getting some idea of the magnitude of the divergencies resulting from different methods of treatment. Air, to a lesser extent, will be included also. This quantity, δ, say, will be the change in c_p per atmosphere relative to its value at one atmosphere, the temperature being constant and taken as 26°C. That is

$$\delta = \frac{1}{(c_p)_0}\left(\frac{\partial c_p}{\partial p}\right)_T \text{ parts per atmosphere} \tag{2}$$

where the subscript 0 refers to a pressure of one atmosphere and T is taken as 299°K. The pressures considered cover a range from 20 to 100 atmospheres.

The result found by Workman for this quantity was

$$\delta = 0.00165 \text{ parts per atmosphere} \tag{3}$$

which exibited no variations greater than the errors of experiment over the entire range of pressures.

Beattie,[3] in computing the heat capacity per mol for air at constant pressure gives the approximation

$$C_p = C_p^* + \left(\frac{2A_0}{RT^2} + \frac{12c}{T}\right)p. \tag{4}$$

The factor in parentheses is equal to the left hand member of Eq. (1) since C_p^* is constant. If we employ the values of the constants for oxygen given by Beattie and Bridgeman,[1] namely, $R=0.08206$, $A_0=1.0763$ and $c=12\times10^4$ and, in addition, the value 6.98 cal. per mol per degree[5] at 26°C, we obtain

$$\delta = 0.00166 \tag{5}$$

The compressibility data of Holborn and Otto[6] offer another means of approach. They are to be found summarized in the form

$$pv = A + Bp + Cp^2$$

where the values of A, B, and C, which are functions of the temperatures only, are each given for 0°C, 50°C, and 100°C respectively. The pressure range goes up from 1 to 80 meters of mercury so that the data are excellent for comparison here. A three-constant formula for interpolation over temperature at constant pressure is required. Fortunately, rather than use a power series of the form

$$pv = d + et + ft^2$$

[5] International Critical Tables, V. 82.

[6] L. Holborn and J. Otto, Zeits. f. Physik **33**, 1 (1925).

a three-constant formula may be derived from the equation of van der Waals

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

which, after terms in the second and higher orders of the small constants a and b are neglected, takes the form

$$pv = bp + RT - \frac{ap}{RT} = g + ht + \frac{k}{273 + t},$$

say, for constant pressure. Any required coefficient in the second formula may be determined from the values of pv at the three given temperatures. The last coefficient only is needed, for

$$T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad \text{may be taken as} \quad \frac{2k}{p(t + 273)^2}.$$

This procedure, when followed out gives

$$\delta = 0.00191 - 2.35 \times 10^{-6} p. \tag{6}$$

Likewise, the result from the power series formula is

$$\delta = 0.00165 - 2.13 \times 10^{-6} p. \tag{7}$$

which, though less valuable, is not without an interest for comparison.

In an earlier paper by the same authors,[7] of which the one just cited seems to be a revision, the quantities A and B are given values identical with those of the later paper, while C is given values one tenth as great at 50°C and 100°C and a value about 0.13 as great at 0°C. The constant term, 0.00191 in Eq. (6) or 0.00165 in Eq. (7) is unaffected but the linear term is greatly affected in proportion to its magnitude. Thus, if the values given in the earlier paper are used as they stand, the term is reduced to a little over one third value, while if, on the other hand, a correcting factor of ten is applied to the earlier paper (making thus eight of the nine values in the two papers agree) the linear term is more than tripled. (It seems possible that the earlier paper contains a misprint).

TABLE I. *Values of* $(1/(c_p)_0)(\partial c_p/\partial p)_T$ *at 26° for oxygen.*

p, atm.	Eq. (3)	Eq. (5)	Eq. (6)	Eq. (7)
20	0.00165	0.00166	0.00186	0.00161
60	.00165	.00166	.00177	.00152
100	.00165	.00166	.00168	.00144

For convenience of comparison, the values of δ as given in Eqs. (3), (5), (6), and (7) are collected in Table I and set down for the mean and extreme pressures under consideration.

[7] L. Holborn and J. Otto, Zeits. f. Physik **10**, 367 (1922).

It appears, first, that the computed and experimental values are of the same order of magnitude; secondly, that the computed values vary among themselves in a way that indicates great sensitiveness to the particular method of treating the data and, by inference, to small variations in the data themselves. In the third place it is quite probable that δ decreases slowly with rising pressure in this part of the field; for, this is indicated by the method of interpolation just employed. Also it is indicated qualitatively by the application of Eq. (1) to an equation of state such as that of van der Waals. On the other hand the absence of variation in the computed column headed "Eq. (5)" is subject to some doubt. For, in a reference, which includes Eq. (4), from which this column is deduced, the author states: "These relations represent the data* surprisingly well; so well, in fact, that some compensation must have taken place between the various approximations made." It follows, fourthly, that the agreement of the values in this column with the experimental values is probably accidental. A final conclusion may be drawn that, if we set down, say, one percent as a reasonable limit to the accuracy now promised by direct experiment such as those of the relative type already referred to it is useless at present to expect calculations from p-v-T data to approach this. One might look forward, in fact, to putting into practice a reversed type of computation applying thermodynamic data in correcting or filling out data on compressibility.

The last conclusion is further borne out by available experimental data and calculations for air. Thus Roebuck[8] gives a table of values for c_p over a field of temperatures and pressures far exceeding that considered here. From his tables one may obtain a mean value

$$\delta_a = 0.00140 \tag{8}$$

where δ_a applies to air instead of oxygen.

From Beattie's computed tables,[3] or Eq. (4), one obtains

$$\delta_a = 0.00165. \tag{9}$$

The constants given for air in the paper just referred to are, however, not all just the same as those given in an earlier paper[1] and repeated in a later paper.[1] This different set, when applied in Eq. (4), gives

$$\delta_a = 0.00146. \tag{10}$$

Bridgeman,[2] on the other hand, using the same equation and the same constants as Beattie but employing a different mathematical treatment, publishes a similar table from which is derived

$$\delta_a = 0.00176. \tag{11}$$

The divergence here is sufficient to bring out the point in question. It is of interest to note, in passing, the way in which the two terms in the parenthesis of Eq. (4) contribute to the values given in Eqs. (9) and (10).

* For air.

[8] J. R. Roebuck, Proc. Am. Ac. Arts Sci. **60**, 537 (1925).

If we consider, as is natural, that the term $2A_0/RT^2$ is representative of molecular attractions, then 62% of the first value and 85% of the second come out as contributions from molecular attractions. This is a further forcible illustration of the sensitiveness of the computed values of thermodynamic quantities to small variations in the value of the coefficients in equations of state arising from small changes in the data themselves or in the processes of adjusting the equations to them.

It should not be overlooked that the calculated values of Beattie and Bridgeman and the experimental values of Roebuck show in the actual magnitude of c_p an agreement much better than might be implied in the foregoing. It is in the differences between values of c_p rather than in the whole quantities themselves that the proportionate irregularities show up the more plainly. Here, indeed, appears again one of the reasons for conducting direct calorimetric experiments.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Relative Efficiency of the Hg-Arc Lines in Exciting the Raman Spectrum of Benzol

The Raman spectrum of benzol was studied by Wood's method, modified to give better results and greater convenience and economy of operation. The Raman tube used was about 30 cm long and 3 cm in diameter, silvered and painted with black Duco on the outside, except for the flat end and a strip about 2 cm wide and 15 cm long, on the side of the tube through which the light of a Cooper-Hewitt 220-volt quartz Hg-arc was permitted to enter. The tube was surrounded by two concentric glass jackets. The innermost one, for solutions of color filters, was omitted when no filters were employed. The outermost tube formed the cooling system. Through it, tap water (whose temperature is very constant in this laboratory) was circulated during exposures. It was found that by omitting the screens and lens usually employed in Wood's method and bringing the flat end of the Raman tube close to the spectrograph slit much better spectra were obtained. The problem of aligning the tube was greatly simplified, and all stray light from the room could be screened off completely by wrapping several layers of black cloth around the end of the Raman tube and slit end of the spectrograph.

The color filters which gave the best results were: 1. Ammoniacal copper sulphate, which transmitted the 4358 and 4047 groups strongly and eliminated the effect of the 3650 group and the 4916, 5461 and 3341 lines; 2. Alcohol solution of quinine sulphate with "Blue Manhattan Lamp Coloring" painted on the outside walls of both filter and water jackets transmitted only the 4358 group. By spreading a thin layer of vaseline over the Duco the chemical acton of the color filters on the paint was effectively prevented.

The Raman patterns for the different exciting lines were charted and found to be complete and identical for the 3650 group and 4047 and 4358 lines, while those for the weaker Hg-arc lines 4108, 4347, 4339 were very incomplete, only the strongest Raman frequency (992) appearing in each case. Many Raman lines coincide with arc lines or other Raman lines. This makes the determination of the efficiency of the exciting lines difficult. Results obtained thus far do not confirm the Fourth Power (Rayleigh) Law in the spectral region 3341–4358. Ornstein and Rekveld report this law to hold for carbon tetrachloride in the region 4047–5461. The higher frequencies appear somewhat more efficient in the excitation of the Raman lines. Equal intensities of incident frequencies are practically equally efficient. The intensities of the lines were measured and calculated by a microphotometer using a carbon ribbon lamp as standard and check well with those of other investigators.

SISTER MAGNA WERTH
University of Minnesota,
September 5, 1930.

Orbital Valency

It has been suggested by Heitler[1] that, in the formation of molecules, the orbital angular momenta may play a rôle analogous to that of the spin angular momenta, in that there is a tendency toward compensation. Just what the precise relationships are, and what special rules hold (as to the order of the molecular terms) for this so-called orbital valency, if it has a meaning, have not been made clear.

[1] W. Heitler, Naturwiss. **17**, 546 (1929).

To investigate the situation, I have studied the problem of the interaction of two identical atoms, each with one p valence electron. These give rise to the following[2] molecular states: $^1\Delta_g$, $^3\Delta_u$, $^1\Pi_g$, $^1\Pi_u$, $^3\Pi_g$, $^3\Pi_u$, $^1\Sigma_u^-$, $^3\Sigma_g^-$, $^1\Sigma_g^+$, $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^3\Sigma_u^+$. These are thus twelve states, and *a priori* it is not evident in what order their energies occur, and which of them correspond to repulsive states. It seems that one must ascertain this by a calculation similar to that of Kemble and Zener[3] for the two-quantum excited states of H_2. This has been done in the present work.

In order to avoid analytical difficulties (and at the same time to follow the work of Zener)[4] an atomic wave-function with the radial part $R(r)=\text{const.}\ re^{-kr}$ has been adopted. Since we are not primarily interested in the absolute values of the energies, but only in their relative positions, it would seem that this assumption is sufficient. A complete treatment would also include other wave-functions but the work has been quite complicated in the above case, which is probably the simplest of all.

When, now, the potential energy for a given value of kR (where R is internuclear distance) is calculated, it is found to be proportional to k, so that the relative positions of the states are not influenced by a change in k. This is true for any function of the form $R(r)=\text{const.}\ r^n e^{-kr}$.

The complete potential energy curves have not as yet been obtained, but for the special value $kR=6$, it is found that the lowest state is a $^1\Sigma_g^+$. The other $^1\Sigma_g^+$, together with $^1\Delta_g$ and $^3\Sigma_g$, are repulsive, while all the remaining states, including $^3\Delta_u$ and the II states, seem to be attractive. Whether any of the states cross each other or not is not as yet known.

A full account of the work, together with various numerical tables will be published as soon as time permits.

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August 30, 1930.

[2] See R. S. Mulliken, Phys. Rev. **36,** 611 and 699 (1930).

[3] E. C. Kemble and C. Zener, Phys. Rev. **33,** 512 (1929).

[4] C. Zener, Phys. Rev. **36,** 51 (1930).

The Probable Number of Isotopes of Eight Metals as Determined by a New Method

In our study of some twenty-five metallic elements in inorganic compounds (Phys. Rev. **35,** 124, 1930; a detailed report of our results is in Press in the *Journal of the American Chemical Society*) we have found that the number of minima of light, or so-called differential time lags, characteristic of each compound is in general the same as the number of known isotopes of the metal. This is true whether the metal be in the chloride, sulphate, nitrate or hydroxide form, a rather extensive series of each having been studied. The same has been found true more recently for several other inorganic salts which we have had the opportunity to study. The method therefore appears to afford a new means of determining the number of isotopes of the metallic elements. It is really to be expected, in the light of our previous experimental results, that each isotope would produce a separate minimum of light corresponding to its mass, for we have found that the positions of the minima of the inorganic compounds are some inverse function of the chemical equivalent of the metallic element of the compound. The scale readings of the minima of the isotopes of a given element, however, appear in general to vary directly with the masses of the individual isotopes, a conclusion which is based upon the order in which the minima characteristic of the given element make their first appearance as the concentration, beginning with extreme dilution, is gradually increased.

It occurred to us to find the number of characteristic minima of some elements of which no isotopes have been reported. We have therefore recently made a study of the elements listed below, finding for each the number of minima indicated.

Gold,	2 minima.
Palladium,	3 "
Platinum,	2 "
Rhodium,	1 "
Ruthenium,	2 "
Tantalum,	3 "
Thallium,	2 "
Thorium,	3 "

If, as seems very probable, our method detects the presence of the isotopes of the metals of inorganic compounds, our results are to be interpreted as showing that the above named

metals have the number of isotopes represented by the number of minima recorded. These elements, for the most part, were studied in the chloride, sulphate and nitrate compounds and the number of the minima for each element was the same in each of the three compounds. Since the relationship connecting scale reading, or time lag, with atomic mass is not known with sufficient accuracy to yield values of atomic masses closer than some two or more units in the case of the foregoing metals, we are unable at present to determine the exact masses of these isotopes. This we believe may be possible, however, with further studies, along with a quantitative estimate of the abundance of the different isotopes.

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The Formation of Striae in a Kundt's Tube

Some experimental work has been carried on by the author from time to time on the formation of striae in a Kundt's tube. An article was written for Nature **118,** 157 (1926) also for Science and School Science and Mathematics the same year setting forth a method of producing these striae by means of a sounding organ pipe.

Since the summer of 1924 observations seemed to show a rotation of the dust particles on each side of the striae and in July 1929 the author succeeded in showing conclusively that such rotation does take place.

A glass tube about 150 cm long and about 2 cm inside diameter had some burned cork scrapings scattered along its inside and a sheet tin piston connected to one prong of an electrically driven tuning fork was used to excite the air vibrations in the tube. The piston was inserted a short distance into the end of the tube and the other end of the tube was closed with a tight fitting cork. When the fork was made to vibrate complete disks of cork dust were produced across the tube at the antinodes and close observation showed that at each disk two distinct orbits of rotating particles were present, one on each side of a single striation, one clockwise, and on the opposite side a counterclockwise rotation. The rotations take place so that the particles leave the top of the striation and enter at the bottom of the same striation. Midway between two adjacent striae little striae lower than the others tend to form but are soon destroyed by the rotations mentioned above, the dust particles forming these lower striae being pulled away in opposite directions and forced into the two adjacent striae at the bottoms of the same. Thus the dust particles are pulled away from a line approximately midway between adjacent striae in opposite directions and forced into the major striae at their bottoms. When the agitation of the dust particles is violent the striae at the antinodes, especially those extending completely across the tube as disks, do not remain always in one position but very often they merge into each other. When the agitation is less violent as in the case were the striae do not extend completely across the diameter of the tube from top to bottom, there seems to be two orbits of rotation on each side of a striation, one above the other, rotating in opposite directions so that the direction of rotation is from near the middle of the striation, one orbit entering the top of the striation, and the other orbit entering the bottom of the striation, somewhat as two meshed cogs one directly above the other, would rotate.

While there seems to be experimental evidence in the scientific literature for the support of the explanation of the formation of striae in a Kundt's tube as given by Koenig, Wied. Ann. t XLII, pp. 353, 549, 1891, the author is inclined to believe that the formation of these striae may be satisfactorily explained in a manner similar to the explanation for the formation of ripple-mark in sand as given by Darwin, Proc. Royal Soc. Vol. 36, p. 18, Oct. 18, 1883.

In the summer of 1927 the author was able to maintain two paper segments, cut in a shape similar to a dust striation, upright in the tube and when pith dust was also present a violent somewhat elliptically shaped rotation about an inch long along its major axis parallel to the axis of the tube, was produced. Also a single segment of paper similar to a dust striation has been maintained upright in the tube for a short time by means of the air vibrations.

In the summer of 1927 striae were obtained by the author by allowing puffs of air produced by interrupting a continuous air stream

from a small glass nozzle by a rotating siren disk and then allowing these puffs to enter a glass tube, one end of which was corked and in which pith dust was distributed along the bottom. These striae were formed when the air jet was interrupted too slowly to produce an audible tone.

The author is continuing his investigation of these striae photographically and is making an effort to determine the effects produced by forming them in various gases and in tubes of various diameters and lengths, and when produced by sources of various frequencies.

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Intensity Changes of Cameron Bands in the Electrodeless Discharge

The band spectra of carbon monoxide obtained in the electrodeless ring discharge have been photographed by the writers under various conditions in order to determine to what extent this source permits controlled excitation, or modification of relative intensities of different band systems. Pronounced intensity changes have been observed, and of these the variations of the Cameron bands are most striking.

The Cameron bands (Phil. Mag. **1**, 405, 1926) were discovered in a discharge tube containing neon and a little CO. They involve transitions from the $^3\Pi$ state which is somewhat metastable, to the $^1\Sigma$ or normal electronic state of the molecule, and are not easy to obtain in emission, although Hopfield and Birge (Phys. Rev. **29**, 922, 1927) without giving details, report finding them in both emission and absorption. Since the initial state has a long life, the bands would be expected to appear only at relatively low pressures, because of the longer interval between impacts. This led Herzberg (Zeits. f. Physik **52**, 815, 1928) to look for them in his careful study of the CO spectra obtained in the electrodeless ring discharge maintained by a damped wave oscillator. Although he kept the gas at quite low pressures, the Cameron bands were not present on his plates.

The oscillator used in the present work is tube driven, with a frequency of about five millions cycles, and a power input variable from about five to one hundred watts. With low power input, the Cameron bands were entirely missing; with increased power they began to appear, and with the highest input they were well developed, with about the same intensity on a microphotometer record as the bands of the fourth positive group lying near them. The exposure in the last case was for 20 minutes, and the pressure was 0.09 mm. Herzberg's excitation apparently is comparable to that of our oscillator with low power input.

Another effect of the high power input was to produce a rise in pressure, in contrast to the decrease or "clean up" obtained with low power. The increase was as much as five fold, far more than could be explained by the rise in temperature. Since there is considerable carbon deposited in the vessel, a release of adsorbed gas from this finely divided carbon, caused by the rise in temperature, must probably be held responsible for the pressure increase.

A quartz spectrograph of low dispersion has been used in searching for intensity changes; since it was proved that the relative intensities of bands can be varied in the electrodeless discharge, it is planned to continue this work with higher dispersion.

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On the Direction of Emission of Photoelectrons from Potassium Vapor by Ultraviolet Light

The wave mechanics (A. Sommerfeld, Atombau und Spektrallinien, Wellenmechanisches Ergänzungsband, p. 213) predicts that the most probable direction of ejection of photoelectrons by polarized light is in the plane of the light beam and the electric vector, the lateral distribution varying as the square of the cosine of the azimuth angle. This has been most satisfactorily shown to be true for light of x-ray frequencies by the well-known experimental work of several investigators.

We have been concerned with examining the same phenomenon in the optical region. Ultraviolet light of wave-length in the region

of 2400A from a monochromator was polarized by a pile of quartz plates and passed through a jet of potassium vapor. A cylindrical grid provided a field-free space in the region of the illuminated vapor so that electrons passed out of the grid in the original directions of ejection by the light. A slit and faraday cylinder arrangement served for the measurement of the number of photoelectrons ejected in various directions relative to the electric vector of the exciting light. Though the energies of ejection were less than one volt-electron, the experiments have clearly shown that the optimum direction is that of the electric vector. Approximately twice as many electrons were observed to be ejected in the direction of the electric vector as at right angles thereto. It seems probable that the electrons observed as ejected at right angles to the electric vector were scattered by the vapor. Correcting for this scattering the observed variation with angle of ejection follows the cosine squared law deduced by Sommerfeld on the basis of the wave mechanics.

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Electrostatic Surface Fields near Thoriated Tungsten Filaments by a Photoelectric Method

The electrostatic fields acting on electrons emitted from a thoriated tungsten filament[1] were studied by the photo-electric method described in a paper by E. O. Lawrence and the writer.[2] The cell was essentially the same as that used in the previous work. In the absence of potassium, a calcium deposit in a side tube immersed in liquid air was used as a getter.

The applied accelerating fields varied from 360 volts/cm, with a corresponding threshold at 4900A (6.1×10^{14} sec^{-1}), to 48,200 volts/cm, with a corresponding threshold at 5500A (5.5×10^{14} sec^{-1}). The apparent reduction in the work function by the increased field was 0.25 volt. This reduction is much larger than was produced by corresponding fields on potassium films, or the reduction which would occur if the Schottky (image force) law held. In the latter case the reduction would be 0.08 volts.

When the fields are calculated, as in the previous work, they are found to approximate the Schottky fields at distances less than 1.5×10^{-6} cm. At 10^{-5} cm from the surface there is a field of about 6000 volts/cm, and at 8×10^{-5} cm from the surface, a field of about 1000 volts/cm. The image fields at these distances are 350 volts/cm and 6 volts/cm respectively. The observed fields are very nearly the same as those Becker and Mueller[3] calculated for 70% thoriated tungsten from thermionic data. The agreement between the two independant methods of determining the fields is striking, and shows that sufficiently large fields are present near thoriated filaments to cause the noted deviations from Schottky's thermionic emission equation.

The hypothesis that the thorium ions exist on the surface in patches[4] which are electropositive with respect to the tungsten, appears best to explain the fields. Electrons emitted through these patches would not only be retarded by the image field, but also by the field between the patches and the ions. A uniform charge distribution on the surface could not cause the observed fields.

The writer intends to continue the studies under different methods of activation before making a detailed report of the work.

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September 9, 1930.

[1] A 4.4 mil thoriated tungsten filament (T122×10) kindly furnished by the Bell Telephone Laboratories, New York.

[2] Lawrence and Linford, Phys. Rev. **36**, 482 (1930).

[3] Becker and Mueller, Phys. Rev. **31**, 431 (1928)

[4] Reference 12 of the paper by Lawrence and Linford lists several articles on the theory of patches.